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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.— Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. — Publisher.

STUDY OF MOLYBDENUM HALIDES

1. VAPOR PRESSURE AND DISSOCIATION PRESSURE OF MOLYBDENUM PENTACHLORIDE

S. A. Shchukarev, I. V. Vasilkova and B. N. Sharupin

Molybdenum halides have received very little study from the thermodynamic point of view; thus, the heat of formation is known only for $MoCl_5$ ($\Delta H^\circ = -90.8$ kcal/mole) [1]; in the case of the remaining halides, there are only the quantities given by L. Brewer [2], for example, for values of their heats of formation by analogy with other substances.

The object of the present work was the study of the dissociation pressure and saturated vapor pressure of molybdenum pentachloride, which have not been studied experimentally and up to this time.

EXPERIMENTAL

For the preparation of molybdenum pentachloride, we used as starting material, chemically pure grade ammonium molybdate. MoO_3 was obtained by calcining the molybdate at 150° until evolution of ammonia, then, for oxidation of the lower oxides, the product was heated to 500° in a stream of oxygen and purified by distillation at 800°.

To obtain molybdenum pentachloride, we used the method of Michael and Murphy [3], using carbon tetrachloride in the chlorination of molybdenum trioxide. The reaction was carried out in sealed glass ampoules at 350°. The molybdenum pentachloride obtained was in the form of glittering black crystals; for purifying from possible admixtures with other chlorides, it was heated in vacuo to 150°.

The substance obtained was analyzed for molybdenum and chlorine contents. The molybdenum was determined by the volumetric method, with the aid of 0.025 N ammonium vanadate solution in presence of phenylanthranilic acid, the chlorine – by potentiometric titration with a 0.05 N silver nitrate solution. The results of the molybdenum pentachloride analyses are given below.

Found %: Mo 35.0, 34.95, 35.10; Cl 64.8, 65.1, 64.9. $MoCl_5$. Calculated %: Mo 35.09; Cl 64.91.

We carried out the determination of the saturated vapor pressure and the dissociation pressure of molybdenum pentachloride by the "flow" method [4-7]. In fitting up the apparatus we took into consideration the following requirements: 1) careful drying of the gas used, made necessary by the tendency of molybdenum pentachloride to hydrolyze slightly; 2) steady flow of inert gas throughout all the experiments and accurate measurement of its volume; 3) constant temperatures throughout the period of the test and their accurate measurement; 4) complete saturation of the gas by the vapor of the substance under investigation.

Nitrogen was used as the inert gas. For purifying it from oxygen, we used copper, heated to 450°; drying was carried out by passing the gas over calcium chloride, anhydrous magnesium chloride and phosphorus pentoxide; residual moisture was removed in a coil immersed in liquid air. First of all, by a series of tests, we established that, for a pressure of the aqueous vapor of $10^{-4}-10^{-5}$ mm Hg, molybdenum pentachloride is practically not hydrolyzed; therefore such a system of drying was regarded as satisfactory.

A constant rate of the stream of nitrogen was controlled by a rheometer and regulated with the aid of constant pressure. The amount of nitrogen passing over the weighed substance at the time of the experiment, was measured with an accuracy of ± 5 ml, which gave an error of not more than 0.5%. Conditions were controlled thermostatically with the aid of an aluminum block and a light-regulated thermoregulator, with an accuracy of ± 0.5°. Temperature was measured by a Pt–Pt, Rh thermometer, with the aid of a PP-1 potentiometer. The speed of the gas throughout the course of all the tests was kept at 6-8 ml/minute. Extrapolation to zero velocity did not result, as preliminary experiments showed, in the fact that, under the test conditions for speeds of gas below 10 ml/minute, the amount of molybdenum pentachloride vaporized does not depend on the speed.

The amount of substance vaporized was determined from the difference in weight of the weighed portion before and after the experiment. Chlorine, which separated on dissociation of $MoCl_5$, was absorbed by potassium iodide solution [8]; then the iodine was titrated with sodium thiosulfate solution. The weight of chlorine was taken into consideration when calculating the amount of molybdenum pentachloride vaporized.

The apparatus was calibrated by the vapor pressure of chemically pure iodine. Errors did not exceed ± 3%.

On heating $MoCl_5$, the following reactions take place:

$$[MoCl_5]_{solid} = (MoCl_5)_{gas} \quad (1)$$

$$MoCl_5 = MoCl_4 + {}^1/_2Cl_2. \quad (2)$$

Apart from this, the possibility of errors was investigated, in the determinations, on account of instability of $MoCl_4$ under the actual conditions. On the basis of Brewer's data [2], $MoCl_4$ may undergo the following changes:

$$MoCl_4 = MoCl_3 + {}^1/_2Cl_2, \quad (3)$$

$$[MoCl_4]_{solid} = (MoCl_4)_{gas} \quad (4)$$

$$2MoCl_4 = MoCl_3 + MoCl_5. \quad (5)$$

Preliminary experiments carried out by us according to the flow method, with $MoCl_4$, showed that at the temperature range 70-160°, the dissociation pressure is less than 10^{-5} mm Hg and, obviously, Reaction (3) does not bring large errors into our measurements.

Measurements of the free energy for Reactions (4) and (5), calculated on the basis of Brewer's data [2], show that Reaction (5) is more profitable from the energy point of view. The data obtained by us also confirm this. The vapor pressure of $MoCl_4$ is low (10^{-4} mm Hg) for the temperature range studied by us, and disproportionation of the reaction in presence of a large amount of $MoCl_5$ vapor, must be suppressed. Thus, Reactions (4) and (5) also do not carry substantial errors into our measurements. The analytical data for molybdenum pentachloride, before and after the experiment, agree among themselves, confirming our suggestion.

TABLE 1

Temperature	P_{MoCl_5} (in mm)	Temperature	P_{MoCl_5} (in mm)
70°	0.10	116°	2.45
80	0.19	116	2.49
98	0.75	123	3.54
98	0.70	135	8.27
108	1.05	150	13.30
115	2.46	162	26.00

The data obtained by us for the process of sublimation are given in Table 1 and are expressed according to the equation $\log P_{MoCl_5} = 10.623 - \frac{3991}{T}$.

In Fig. 1, apart from our data, data calculated on the basis of appraised figures adopted by Brewer [2], are included; as seen, they agree very well with ours.

On the basis of the figures obtained experimentally for the saturated vapor pressure of $MoCl_5$, the thermodynamic functions were calculated, as characteristics of the sublimation process (Table 2).

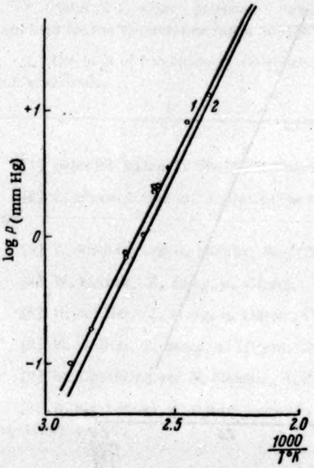

Fig. 1. Pressure of saturated vapor of molybdenum pentachloride. 1) Our data, 2) Brewer's data.

TABLE 2

	Experimental data	Evaluated figures, Brewer's data
ΔH^0	18.3 kcal/mole	20.8 kcal/mole
ΔS^0	35.6 energy units	40.5 energy units
ΔF^0	7.7 kcal/mole	8.4 kcal/mole

$MoCl_5$ may be dissociated in the solid as well as in the gaseous state:

$$[2MoCl_5]_{solid} = 2[MoCl_4]_{solid} + Cl_2, \quad (6)$$

$$2(MoCl_5)_{gas} = 2[MoCl_4]_{solid} + Cl_2. \quad (7)$$

In the first case the equilibrium constant is equal to $K'_{eq} = P_{Cl_2}$, in the second $K''_{eq} = \frac{P_{Cl_2}}{P^2_{MoCl_5}}$.

The values obtained by us, K'_{eq} and K''_{eq} given in Table 3 and in Figs. 2 and 3.

The value of the equilibrium constant is expressed by the equations:

$$\log K'_{eq} = 14.143 - \frac{5412}{T},$$

$$\log K''_{eq} = -6.753 + \frac{2448}{T}.$$

TABLE 3

Temperature	$K'_{eq.}$	$K''_{eq.}$	Temperature	$K'_{eq.}$	$K''_{eq.}$
98°	0.35	0.72	116°	2.32	0.37
98	0.33	0.59	123	4.08	0.33
108	0.59	0.53	150	18.30	0.10
115	2.18	0.36	162	39.50	0.06

On the basis of the values K'_{eq} and K''_{eq}, the following thermodynamic quantities were calculated for Reactions (6) and (7).

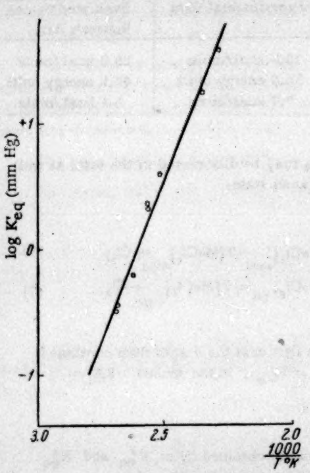

Fig. 2. Equilibrium constant of reaction $2\,[MoCl_5]_{solid} = 2\,[MoCl_4]_{solid} + Cl_2$.

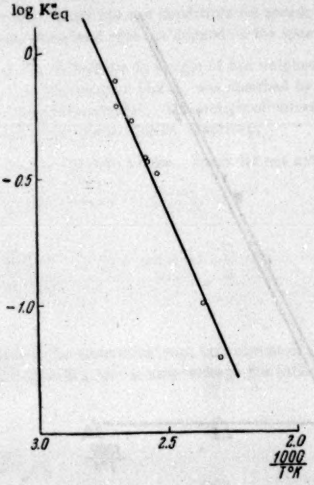

Fig. 3. Equilibrium constant of reaction $2\,(MoCl_5)_{gas} = 2\,[MoCl_4]_{solid} + Cl_2$.

TABLE 4

	$2\,[MoCl_5]_{solid} =$ $= 2\,[MoCl_4]_{solid} + Cl_2$	$2\,(MoCl_5)_{gas} =$ $= 2\,(MoCl_4]_{solid} + Cl_2$
ΔH^0	24.5 kcal/mole	−12.3 kcal/mole
ΔS^0	49.2 energy units	50.2 energy units
ΔF^0	9.9 kcal/mole	2.6 kcal/mole

TABLE 5

$MoCl_4$	From Reaction (6)	From Reaction (7)	Brewer [2]
ΔH^0_{form}	−78.5 kcal/mole	−78.6 kcal/mole	−79 kcal/mole

On the basis of our experiments, the assumption may be put forward that dissociation of $MoCl_5$ at low temperatures proceeds predominantly in the gaseous state.

In Table 4 are given the heats of formation of $[MoCl_4]_{solid}$ (Table 5), calculated for the dissociation processes.

SUMMARY

1. Saturated vapor pressures and dissociation pressures of molybdenum pentachloride have been determined for the temperature range 70-160°.

2. The heat of formation of molybdenum tetrachloride has been calculated and is equal to −78.5 kcal/mole.

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CHEMISTRY OF COMPOUNDS OF VARIABLE COMPOSITION

II. LATTICE ENERGY OF ACIDS OF ELEMENTS OF SUBSIDIARY SUBGROUPS

S. M. Ariya, E. Volf, G. Grossmann and M. P. Morozova

Earlier [1], on the basis of an investigation of the equilibrium $FeO_{1+x+y} + yCO \rightleftharpoons FeO_{1+x} + yCO_2$ we established the dependence of the enthalpy of formation of ferrous oxide on composition, within the limits of the homogeneous field.

It is known [2], that ferrous oxide forms a lattice of the sodium chloride type, in which (depending on the thermodynamic conditions under which the compound exists) some portion of the positions in the cation lattice is empty. The corresponding portion of iron ions has a charge of + 3, which guarantees the electrical neutrality of the lattice. In other words, the composition of ferrous oxide may be represented by the formula $Fe^{+2}_{1-3x}Fe^{+3}_{2x}\otimes_x O_{1.00}$, where $\otimes$ signifies a vacant position in the cation lattice. Hitherto, many authors have considered that the free positions and ions with increased charge are arranged in the lattice quite irregularly, from the statistical point of view.

We determined the magnitude of the lattice energy of ferrous oxide of varying composition, on the supposition of a statistically disordered distribution of free positions and triply charged iron ions.

As known, the magnitude of the energy of the ionic lattice of a compound of the type $A^{+2}B^{-2}$, according to Born's theory, is represented by the formula (for lattices of cubic form):

$$E=\frac{NA\alpha^2e^2}{l}\left(1-\frac{1}{n}\right), \tag{1}$$

where E is the lattice energy in the gram-formula, α is the quotient of the ion charge to the electron charge, e is the electron charge, l is the boundary line of the elementary nucleus, n is the index of repulsive force, A is the Madelung constant and, for the NaCl type lattice, is equal to 3.495115.

In an NaCl type lattice, each ion is immediately surrounded by six oppositely charged ions (at a distance of $l/2$); then follows a concentric layer of 12 similarly charged ions (at a distance of $\frac{1}{2}\sqrt{2}$); then 8 oppositely charged ions (at a distance of $\frac{1}{2}\sqrt{3}$); 6 similarly charged ions (at a distance of $\frac{1}{2}\sqrt{4}$); •24 oppositely charged ions (at a distance of $\frac{1}{2}\sqrt{5}$); etc.

The energy of electrostatic interaction of an oxygen ion with the remaining ions in the lattice can be expressed in the following manner in accordance with what has just been said (for an ideal iron oxide lattice of stoichiometric composition):

$$\varepsilon=\frac{8e^2}{l}\left(\frac{6}{\sqrt{1}}-\frac{12}{\sqrt{2}}+\frac{8}{\sqrt{3}}-\frac{6}{\sqrt{4}}+\frac{24}{\sqrt{5}}+\dots\right). \tag{2}$$

Let us assume that free positions which appear at a concentric layer of a circle of a given oxygen ion, are compensated by these triply charged ions which arise within the limits of the same layer (i.e., the appearance of one free position is accompanied by the appearance of two triply charged iron ions, in the same layer). Now, for example, in the fifth layer one free position appears and correspondingly, two Fe^{+3} ions. The energy of interaction of an O^{-2} ion with ions composed of Fe^{+2} (in number 21) amounts to: $\frac{8e^2\cdot 21}{\underline{l}\sqrt{5}}$.

To this must be added the energy of interaction of this same ion with two Fe^{+3} ions, which is equal to $\frac{12e^2\, 2}{\underline{l}\sqrt{5}}$. The sum of both terms comprises an amount which is present in the ideal lattice of ferrous oxide $\frac{8e^2\cdot 24}{\underline{l}\sqrt{5}}$. Thus, the appearance of Fe^{+3} ions and vacant positions in one and the same concentric layer does not alter the magnitude of the lattice energy.

For the appearance of a free position in one concentric layer with reference to a given ion, and of Fe^{+3} ions in other concentric layers, naturally, the quantity given in brackets in Equation (2), varies. However, for statistical distribution of lowered and raised values, this quantity must be mutually compensated. In other words, the energy of interaction of oxygen ions with all residual ions in the lattice must not be changed for partial substitution of Fe^{+2} ions in the vacant positions and Fe^{+3} ions in corresponding correlation (produced under neutral conditions of the lattice).

With reference to the energy of interaction of iron ions with all residual ions in the lattice, this quantity does not vary when "defects" are produced in the lattice. Actually, as already stated above three Fe^{+2} ions are replaced by one free position and two Fe^{+3} ions. A decrease in the number of Fe^{+2} ions by three results in a decrease in the lattice energy by the amount:

$$3\cdot\frac{8e^2}{l}\left(\frac{6}{\sqrt{1}}-\frac{12}{\sqrt{2}}+\frac{8}{\sqrt{3}}-\frac{6}{\sqrt{4}}+\frac{24}{\sqrt{5}}+\ldots\right),$$

but the energy of the reaction arising by exchange of two Fe^{+3} ions, comprises the amount:

$$2\cdot\frac{12e^2}{l}\left(\frac{6}{\sqrt{1}}-\frac{12}{\sqrt{2}}+\frac{8}{\sqrt{3}}-\frac{6}{\sqrt{4}}+\frac{24}{\sqrt{5}}+\ldots\right).$$

Thus, the electrostatic composition of the lattice energy with variation in composition of ferrous oxide, must vary only in agreement with the variation in lattice parameter. With reference to the energy of the repulsive force, this must vary, but by an insignificant amount.

As is known, the usual magnitude of the repulsive energy depends on the number of ions situated relatively close to each other, since the repulsive force quickly falls, practically to zero, according to the extent of the withdrawal of the ions from each other.

The appearance of free positions in the lattice naturally attracts to it a decreased number of ions surrounding each given ion; correspondingly, the absolute amount of this lattice energy is decreased.

The usual magnitude of the lattice energy of ferrous oxide is more than 900 kcal for n equal to 8; the energy of the repulsive force accounts for 1/7 of this amount, i.e., about 135 kcal.

In passing from a lattice of composition FeO to a lattice $Fe_{0,9}O$, the usual number of ions in the lattice is increased by 1/20; the magnitude of the repulsive energy must be decreased by approximately this amount, i.e., it may be assumed that the usual figure for the lattice energy must be increased in all by 6-7 kcal.

TABLE 1

Dependence of Lattice Parameter of Ferrous Oxide on Composition.

Formula	Lattice parameter
$Fe_{0.9113}O$	4.2816
$Fe_{0.9175}O$	4.2847
$Fe_{0.9286}O$	4.2900
$Fe_{0.9316}O$	4.2920
$Fe_{0.9440}O$	4.3010

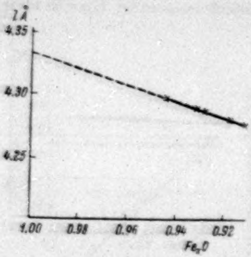

Fig. 1. Dependence of lattice parameter of ferrous oxide ($\underline{l}$) on composition (in A).

The dependence of the lattice parameter of ferrous oxide on composition is given in Table 1 (according to data [2]), and in Fig. 1.

As seen from Fig. 1, the lattice parameter is shown to be a practically linear function of composition. This circumstance, in combination with Schenk's data [3] shows that the ratio $\frac{P_{CO_2}}{P_{CO}}$ for a "re-reduced" ferrous oxide, up to the stoichiometric composition (FeO) varies to the same extent as in the thermodynamics of the stable field of its existence, and gives us a basis for extrapolation to a straight line (Fig. 1) up to the composition FeO; $\underline{l}$ is shown for this to be equal to 4.332.

On the basis of the above, with reference to the magnitude of the lattice parameter of ferrous oxide, values were calculated according to Formula (1) for the energy of the lattice of ferrous oxide of varying composition and are given in Table 2, which includes values for the enthalpy of formation of ferrous oxide of varying composition, obtained from them with the aid of the circulating process. The graph following this table contains the values found experimentally for the enthalpy of formation of ferrous oxide (the figure for FeO was obtained by extrapolation).

TABLE 2

Composition of ferrous oxide	Lattice energy (kcal/gram-formula)	Enthalpy of formation	
		Calculated on gram-formula	Determined experimentally
FeO	930.8	68.1	62.7 (extrapolation)
$Fe_{0.9466}O$	937.7	43.7	63.1
$Fe_{0.9113}O$	942	26.0	63.5

The calculated and experimentally determined results of the enthalpy of formation of ferrous oxide are represented graphically in Fig. 2 from which it is seen that if, for a composition of FeO, the calculated amount lies close to the experimental, then, according to the extent of increase of comparative oxygen content, neither the absolute amounts, nor the course of the enthalpy of formation are passed on to the calculation based on the suggestion relating to the statistical distribution in the lattice of free positions and Fe^{+3} ions.

In 1952, Bertaut [4], showed that, arising from the electrostatic composition of the energy of the lattice, the statistically disordered distribution of free positions and ions increased by the charge on the salt-formed compounds of varying composition, is not an advantage.

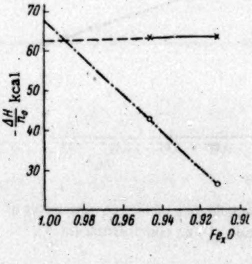

Fig. 2. Experimentally found and calculated dependence of enthalpy of formation of ferrous oxide, relative to 1 g-atom of oxygen (in kcal), as a function of the composition of the solid phase. Continuous line – found experimentally, dash-point – calculated.

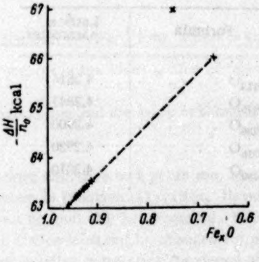

Fig. 3. Enthalpy of formation of iron oxides relative to 1 g-atom oxygen as a function of composition (in kcal).

In agreement with the calculations of Bertaut, free positions and ions of increased charge must be distributed in the lattice regularly and actually; in such a manner that there would possibly be free positions further from each other, and ions with increased charges would possibly be situated nearer to them.

The results obtained by us in this way, do not contradict Bertaut's considerations.

Bertaut [5], obtained x-ray data which indicated the ordered distribution of free positions in the lattice of pyrrhotite (FeS_{1+x}). It is true that Benoit [6], assumed that this ordered distribution is present only at relatively low temperatures, being transformed at raised temperatures to statistically disordered distribution.

Our data relating to the enthalpy of formation of ferrous oxide of varying composition, were obtained on the basis of measurements of the equilibrium at high temperatures; it is possible that this means that, at high temperatures an ordered distribution is present, in the lattice of ferrous oxide, of vacant positions and Fe^{+3} ions. Of course, the explanation is still not complete and does not give any conclusions about the ions of better known models for the common location in the lattice of Fe^{+2} and Fe^{+3} ions, side by side with the vacant positions.

If we compare the enthalpy of formation of ferrous oxide of varying composition with the enthalpy of formation of mixtures (those of empirical composition), poor in oxygen, of ferrous oxide and ferric oxide, then they are shown to be practically the same.*

The course of the enthalpy of formation of iron oxides is given in Fig. 3, from which it is seen that the Fe_3O_4 point lies appreciably above the additive straight line. In Figs. 4 and 5 the magnitudes of the enthalpies of formation of oxides in the systems Ti–O, W–O, relative to 1 g-atom of oxygen, are given. It is quite obvious, for example, that the enthalpy of formation of Ti_3O_5 is practically no different from the enthalpy of formation of mixtures of Ti_2O_3 and TiO_2, the enthalpy of formation of $WO_{2.7}$ does not differ appreciably from the enthalpy of formation of mixtures of WO_2 and WO_3.

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* Later we established that the enthalpy of formation of titanous oxide TiO_{1+x}, is not very different in practice from the enthalpy of formation of mixtures of TiO and Ti_2O_3, of the same empirical composition.

In $WO_{2.7}$, evidently the tungsten occurs in those valency states which we have, on the one hand, in WO_2 and on the other hand, in WO_3. The same may be said of Ti_3O_5, Ti_2O_3 and TiO_2, respectively.

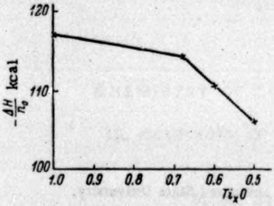

Fig. 4. Enthalpy of formation of titanium oxides, relative to 1 g atom of oxygen (in kcal), as a function of composition.

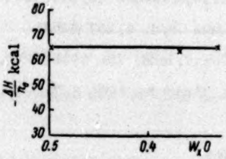

Fig. 5. Enthalpy of formation of tungsten oxides, relative to 1 g atom of oxygen (in kcal) as a function of composition.

Unfortunately, up to the present we have not located by accurate data, details of the structure of Fe_{1+x}, Ti_3O_5 and other intermediate oxides, investigated thermodynamically, but may suggest here that we are recording an approximation of the enthalpy of formation of intermediate oxides and mechanical mixtures of corresponding oxides, which is explained by the fact that in the lattice of intermediate oxides, there are elements of the structure of both the limiting oxides. In other words, it may be considered that in the lattice of intermediate oxides, atoms of the metal are contained in varying states of valency, each atom situated in a corresponding valency state having the same, or approximately the same, boundary as in the limiting oxide corresponding to this valency state.

Fe_3O_4 is excluded from the systems examined. As is known, there are indications in its lattice of the presence of atomic links; in any case, the physical properties of Fe_3O_4 are obviously specific.

It is understood that further coupling of the experimental data on the enthalpy of formation of intermediate oxides of elements of subsidiary subgroups is necessary; however it is now quite obvious that the examples given here cannot be accidental.

Taking into consideration the equality of the enthalpy of formation of compounds with the enthalpy of formation of mixtures of two different compounds of the same system, or mixtures of compounds with a simple substance (of the same empiricial composition) frequently observed in intermetallic systems [7], it may be suggested that the regularity noticed is of a sufficiently general character.

SUMMARY

1. It is shown that the magnitude of the enthalpy of formation of ferrous oxide of varying composition, calculated on the assumption of statistically disordered distribution in the lattice of free positions and Fe^{+3} ions, according to its absolute meaning, as well as according to the trend of its variation in composition, does not agree with the experimental findings. Probably this is explained by the regular distribution of free positions and Fe^{+3} ions in the lattice.

2. It is established that the enthalpy of formation of ferrous oxide of varying composition is probably no different from the value of the enthalpy of formation of mixtures of ferric oxide and ferrous oxide, poor in oxygen.

3. In examples of the systems Fe–O, Ti–O, W–O, it is shown that the enthalpies of formation of oxides containing elements of subsidiary subgroups in two valency states are practically the same as the values for the enthalpy of formation of mixtures of these two oxides, each of which contains a corresponding element in one of the two valency states contained in the intermediate oxides examined. Oxides of the spinel type are excluded.

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CHEMISTRY OF COMPOUNDS OF VARIABLE COMPOSITION

III. COMPOUNDS OF VARIABLE COMPOSITION AND THE PERIODIC LAW

S. M. Ariya, E. Volf and G. Grossmann

In principle, any compound with a nonmolecular lattice, has a definite field of homogeneity [1], however, very often these fields of homogeneity are so narrow, that, for the present position of methods of investigation, the corresponding substances are regarded as compounds of constant composition. However, in a large number of cases the chemical compound is characterized quite appreciably, and sometimes to a significant extent, by the composition axis. It is natural that the presence of one or another field of homogeneity of a chemical compound is represented as one of its important properties. It is therefore natural to examine how this property varies for binary compounds in the periodic system. It is understood that the magnitude of the field of homogeneity is a function of many parameters and therefore it is difficult to expect very simple rules for its variation in passing from one element to another in the periodic system. In the present communication we have only examined metal – nonmetal compounds, excluding for the present, intermetallic compounds.

First of all we must emphasize that the range of composition for which the chemical compound can exist in a state of thermodynamic equilibrium is shown to be a function of the properties not only of this compound, but also of the properties of the corresponding system of the two elements on the whole. Thus, for example, ferrous oxide, at 900° has a field of homogeneity in the composition range $FeO_{1.04}$ - $FeO_{1.11}$ [2], by reason of the fact that the homogeneous oxide of composition $FeO_{>1.11}$, has, at this temperature, an oxygen pressure in excess of the equilibrium pressure of oxygen over Fe_3O_4; therefore the compounds indicated must begin to form for an excess chemical potential of oxygen, in the surrounding oxide medium, in the sense corresponding to the existence of an $FeO_{1.11}$ equilibrium. Similarly, the suggestion of a low limit for the field of homogeneity of ferrous oxide depends on the fact that the free energy of a mixture of $FeO_{1.04}$ and an oxoferrite of corresponding composition (a solid solution of oxygen in iron), has a lower free energy, $FeO_{<1.04}$. In other words, the location on the composition axis of the limit of existence of the ferrous oxide equilibrium is determined not only by the properties of this oxide but also by the properties, on the one hand, of the oxoferrite and on the other hand, of ferrous-ferric oxide. This circumstance is not always taken into consideration by the crystallo-chemists (to whom we are mainly indebted for our knowledge of compounds of variable composition), who have frequently endeavored to explain the presence in compounds of this or that field of homogeneity exclusively by the properties of the lattice of this compound.

On examining the dependence of the magnitude of the field of homogeneity of binary compounds on the position of the elements in the periodic system, it is necessary to again follow one observation. The absolute majority of data on the magnitude of the fields of homogeneity are obtained in the course of x-ray investigations. As a rule the taking of an x-ray of preparations is carried out at room temperature. As the temperature at which hardening proceeds in the solid substance is not known, and may vary for different cases, then the data at our disposal, strictly speaking, are not comparable. If we add to what has been said the fact that x-ray methods are not often very sensitive, then there is the explanation that we may not bother about a few variations in the magnitude of the field of homogeneity on transferring from one compound to another. The most reliable information on the extent of the field of homogeneity of chemical compounds may be obtained in the course of thermodynamic investigations however there has been very little work in this field, up to now.

Turning to the basic contents of the present communication, it should first of all be mentioned that appreciable fields of homogeneity are observed only for compounds of elements of subsidiary subgroups. There have been indications in the literature of the existence of fields of homogeneity for lead oxides which have been disputed hitherto. Figure 1 illustrates the course of the magnitude of fields of homogeneity of compounds of elements of the first decade. The data given are taken mainly from the literature [3]. The data for manganous oxide were obtained by us. E. Ya. Rode [4], and a number of other authors, have shown that oxidation of manganous oxide at low temperatures leads to formation of products whose powdergrams are distinguished from those of manganous oxide only by a washed-out appearance of the line. The magnetic properties of these substances which contain oxygen approximating to the formula $MnO_{1.15}$, do not contradict the suggestion that addition of oxygen is accompanied by an increase in valency of part of the manganese atoms. These substances received the name of manganasite solid solutions. It is not clear whether they represent their own product of absorption of oxygen or partial oxidation to Mn_2O_3, manganous oxide. The pressure of oxygen above them is appreciably higher (in some of the series) than the pressure of oxygen above Mn_3O_4 (for one and the same temperature), i. e., in any case where they might be of the nature of manganasite solid solutions, they represent specific thermodynamically unstable substances, which it is therefore impossible to compare with fields of homogeneity of oxides of titanium, iron, etc., situated in a state of thermodynamic equilibrium with adjacent compounds, according to their oxygen content. For elucidating the nature of the thermodynamic equilibrium of the field of homogeneity of manganous oxide, mixtures of it with varying amounts of Mn_3O_4 were sintered continuously for 30-40 hours in high vacuum at 700-900°. Accurate x-ray photographs were taken of the preparations obtained and showed that the lattice parameter of manganous oxide entering into the composition of the preparation of empirical composition $MnO_{1.07}$ in which Mn_3O_4 has already been detected by x-rays, coincides with a lattice parameter of manganous oxide in the preparation $MnO_{1.00}$.

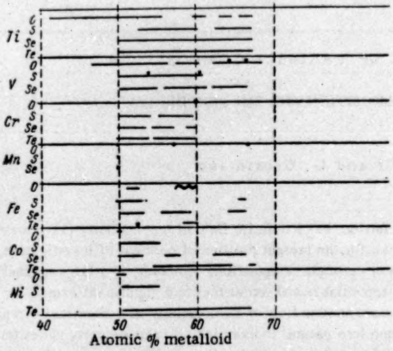

Fig. 1. Magnitude of the field of homogeneity of some compounds of elements of the first decade.
(wavy line shows unstable field of homogeneity
γ-Fe_2O_3).

Thus, we found: for the preparation $MnO_{1.00}$ $\underline{a} = 4.433 \pm 0.001$ kx;. for the preparation of empirical composition $MnO_{1.07}$ $\underline{a} = 4.431 \pm 0.001$ kx.

Apart from this, we studied the interaction of manganous oxide with CO_2-CO mixtures at 700° with the aid of the circulation apparatus described earlier. It was shown that enriching the gaseous mixture with carbon dioxide up to the ratio p_{CO_2}/p_{CO} equal to 70 does not bring about addition of oxygen to MnO. It may be seen from this that manganous oxide possesses only an inappreciably small field of homogeneity. Thus, compounds of manganese occupy a special position among compounds of elements of the first decade. This, of course, is connected with the special structure of the electronic surface of the manganese atom, which has half the total d-surface. Some of the manganese nitrides have been characterized by observing fields of homogeneity; however, these compounds approximate intermetallic compounds in specific character, which we are not examining here.

On passing into the secondary subgroups, there is observed on the whole, from top to bottom, as illustrated in Fig. 2, a tendency to decreased magnitude of the field of homogeneity. There are, however, exceptions to this rule. Thus, for example, the fields of homogeneity of higher oxides are sometimes distributed in the subsidiary subgroups for increased series number. There may also be shown for selenides of vanadium and tantalum, the field of homogeneity of tantalum selenide $TaSe_{1.8}$ − $TaSe_{2.8}$; in this composition range, in the system V−Se, there are three compounds, the fields of homogeneity of which apparently are not linked. Attention has been drawn to the fact of the absence of appreciable fields of homogeneity of halides of elements of subsidiary subgroups.

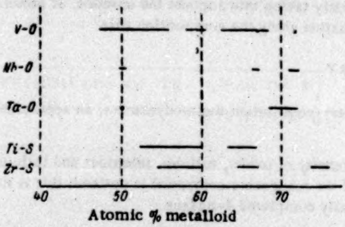

Fig. 2. Magnitude of fields of homogeneity of compounds of subsidiary subgroups of the periodic system.

Fields of homogeneity of binary compounds may be distributed as solid solutions of one compound (existing or not existing in the free position) linked in others (also existing or not existing in the free position). As known, the assumption was confirmed a long time ago, that "like dissolves in like." From this point of view we may attempt to find signs of similarities in compounds of different composition in one and the same binary system, which might guarantee the possibility of formation of homogeneous solid solutions. It is known that the rule justified itself in clarifying the mutual solubility of metals with each other, since it required, in order to distinguish radii of atoms from each other, no more than some definite portion. Application of this rule to compounds of one and the same element in different valency states is not very satisfactory, since so-called ionic radii do not exhibit specific constants for a given element in a given valency state, the figures being a function of the properties of the second element, such as coordination number, etc. As a result of the similar criteria for two different compounds of the same two elements guaranteeing the possibility of the formation of solid solutions, by them, we attempted to utilize their energy characteristics. In this connection, we took the value of the isometalloid enthalpy of formation, i.e., the enthalpy of formation relative to 1 g-atom of the nonmetallic element [5]. The course of the isometalloids are shown in Fig. 3, in the systems Fe−O and Fe−Cl. Ferrous oxide, as indicated above, has a sufficiently wide field of homogeneity − the isometalloid (isoxygen) in this system has a very smooth course; the absence of appreciable fields of homogeneity of iron chlorides, on the contrary, corresponds to a very steep course of the isometalloid (isochlor). In Fig. 4 is represented the course of the isometalloid (isoxygen) for the systems Fe−O and Mn−O. The absence of an appreciable field of homogeneity for manganous oxide, contrary to ferrous oxide, corresponds to an appreciably great steepness in the curve of the isoxygen in the Mn−O system, compared with the Fe−O system.

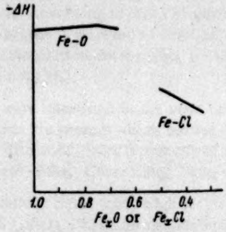

Fig. 3. Dependence of isometalloid enthalpy of formation of iron oxides and chlorides on the composition of the compounds.

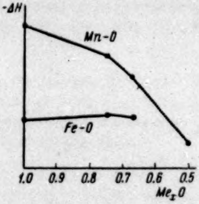

Fig. 4. Dependence of isoxygen enthalpy of formation of oxides of iron and manganese on the composition of the compounds.

We checked this rule for those cases for which corresponding data are available, and it applied to all cases when an examination was made of the existence of a field of homogeneity for a range of composition lying between the different compounds. For the composition range lying between metals and their lower oxides, this rule does not apply. Of course this rule does not express the causative link, it represents a specific correlation however, which is apparently sufficiently stable and powerful to be used for practical evaluation of the magnitude of the field of homogeneity in binary systems, particularly taking into account the absence, at present, of other means of determining the extent of chemical combination along the composition axis.

SUMMARY

1. It is established that manganous oxide does not possess (equilibrium thermodynamics) an appreciable field of homogeneity.

2. On examining the magnitude of the fields of homogeneity of oxides, sulfides, selenides and tellurides of elements of the first periodic group, the special position of the manganese compound is noticed; this is situated in association with existence, in atoms of this element, of a fully completed d-surface.

3. Broad fields of homogeneity are observed, as a rule, in those systems in which there is a sloping course of the isometalloid enthalpy of formation.

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PRINCIPLES OF TRANSFER OF METALS IN A VOLTAGE SERIES IN SOLVENTS WITH LOW DIELECTRIC CONSTANTS

E. Ya. Gorenbein

I. As is known, transfer of metals in a voltage series is easily carried out in aqueous solutions only when ions in equilibrium with a reverse electrode are linked in complex compounds in which they display complex formation. As a result, potential-determining ion concentration is suddenly decreased and the electrode having a positive charge in the galvanic element may remain negative, i.e. under these conditions the metal is displaced in the voltage series. This effect takes place in aqueous as well as nonaqueous solutions and is in agreement with the laws of dilute solutions. However, a number of cases have been observed, particularly in solvents of low dielectric constant, when metals are displaced in a voltage series and the potential-determining ions enter into the composition of complex compounds and are located in the external zone. It is thought that under these conditions, concentration of "simple" ions is not decreased and must increase the more rapidly as electrostatic interaction decreases.

It is quite obvious that the explanations given for cases where potential-determining ions undergo complex formation cannot be applied to conditions, where, in spite of complex formation, potential-determining ions are in the outer zone. Up to now no attention has been given to this.

Research workers who have studied displacement of metals in a voltage series, saw only one fact, – displacement of metals in this series – and this appeared to be satisfactory to them for transferring the general explanation which is true for certain cases to all cases of displacement of metals in a voltage series. In view of the fact that transfer of metals in a voltage series is mainly observed in solvents of low dielectric constant, and taking into consideration the fact that in the majority of the systems studied the electrolytes comprise complexes of aluminum halides, we undertook these investigations.

II. According to thermal analysis data, aluminum bromide forms complex compounds with bromides of other metals [1], which are good electrolytes like aluminum bromide itself [2] in other organic [3] and inorganic [4] solvents. According to other properties which have been studied, in a number of cases the composition of these compounds is retained in solution. Moreover, some compounds have been isolated from nonaqueous solutions and their composition determined, for example, $CuBr \cdot AlBr_3$, $LiBr \cdot AlBr_3$, $AgBr \cdot AlBr_3$, $KBr \cdot AlBr_3$ [5], $SbBr_3 \cdot AlBr_3$ and $BiBr_3 \cdot AlBr_3$ [6].

We were interested in the need for establishing some sort of structure for these compounds in the composition of which ions are present which are the opposite with reference to the corresponding electrodes, the metals of which are displaced, most frequently of all, in the voltage series. To them belong the following complex compounds: $AgBr \cdot AlBr_3$, $CuBr \cdot AlBr_3$, $HgBr_2 \cdot Al_2Br_6$, $SbBr_3 \cdot AlBr_3$, $BiBr_3 \cdot AlBr_3$ and some others.

Aluminum has a fairly high ionization potential [7], the aluminum ion generating a very strong pole. This undoubtedly offers a basis for maintaining that in these compounds the aluminum ion proceeds to complex formation. If we start from the new ideas about acid – base interaction, then, in the preceding compounds, aluminum must enter into the composition of a complex anion, in which there is a central atom. These theoretical considerations agree completely with electrical investigations of these complexes in various nonaqueous media.

Investigations of the transfer number [8] confirm absolutely that metals separating at the cathode, on electrolysis of the compounds enumerated, are located in the outer zone of the complexes under examination.

On this basis, V. A. Izbekoff [8], visualized the structure of these complex compounds as follows: Ag [$AlBr_4$], Hg [$AlBr_4$]$_2$, Cd [$AlBr_4$]$_2$, Sb [$AlBr_6$],etc.

Such a structure arises from the coordination numbers which aluminum possesses. As known, in aluminum the coordination numbers mostly correspond to four and six.

If attempts are made to represent these compounds with aluminum in the outer zone as a result of the known coordination numbers for $Ag^{\cdot}$ and $Cu^{\cdot}$, equal to two;and for $Hg^{\cdot\cdot}$ and $Cd^{\cdot\cdot}$, equal to four; then such a structure for the complexes does not agree with experimental data relating to their composition.

It follows from this statement that, on investigating transfer of metals in the voltage series, when the electrolytes are complex compounds of aluminum halides, potentialial-determining ions in these compounds are located in the outer zone.

III. Let us examine the experimental data relating to such systems in which the electrolytes are complex compounds of aluminum bromide and dielectric solvents (nonelectrolytes).

V. A. Izbekoff [9], studied the decomposition voltage of bromides of some metals in aluminum bromide as solvent and on the basis of the data obtained placed the metals in the following voltage series: Al, Zn, Cd, Ag, Hg, Sb, Bi.

This series is quite different from the voltage series in aqueous solutions: Al, Zn, Cd, Sb, Bi, Ag, Hg.

The voltage series obtained in the work [9], was expanded greatly by Yu. Delimarsky and V. A. Izbekoff [10]. The authors carried out investigations in exactly the same solvent in presence of potassium bromide; decomposition voltages and individual electrode potentials were measured at the same time. The following series was obtained: Tl, Al, Zn, Pb, Cd, Sn, Ag, Cu, Fe, Hg, Co, Ni, Sb, Bi. Attention is drawn to the fact that the order of metals in the voltage series did not vary in pure $AlBr_3$ and for investigations of the system $KBr-AlBr_3$.

E. M. Skobets and N. S. Kavetsky [11], established a voltage series for metals, the bromides of which were soluble in the system $NaBr-AlBr_3$ (30 mole % NaBr) by measuring the emf of the circuit, using a glass-sodium electrode (sodium amalgam || glass).

The series (Al, Zn, Cd, Pb, Sn, Ag, Bi, Cu, Hg) obtained by these investigations differs* from that obtained in a pure $AlBr_3$ melt, in that bismuth is shown in the series before copper and mercury.

Yu. K. Delimarsky and A. A. Kolotti [12], measured the decomposition voltage of those bromides which had been studied earlier by Izbekoff and Delimarsky [10] (thallium bromide was replaced by manganese bromide); a complex of equimolecular composition – $NaBr \cdot AlBr_3$, was shown by the solvent. Measurements were carried out at high temperatures (260-500°) using glass diaphragms. The voltage series, as was to be expected, was no different when compared with the series obtained for metal bromides in the system $KBr-AlBr_3$, the only difference being that silver was found before copper. It is possible that this was a result of the different temperatures of the tests (105, 260-500°) and the concentration of silver and copper bromides, since in the first case a mixture of aluminum and potassium bromides (13 % KBr and 87% $AlBr_3$) was used, corresponding to the molecular composition $KBr + 3AlBr_3$ [10], and in the second case – to the composition $NaBr + AlBr_3$ [12]. However, in the article by Yu. K. Delimarsky [13], without any reservations an experimental temperature of 105° was used instead of 360°, and instead of a mixture composition $KBr + 3AlBr_3$, a composition corresponding to the complex $KBr \cdot Al_2Br_6$ was used; in this case copper was found before silver, in the voltage series (see Table 3 in the article quoted [13], in spite of the fact that, in work published earlier [10], copper stands after silver).

We draw attention to this since further on we shall examine the effect of the dielectric on the displacement of metals in the voltage series, in conjunction with other physicochemical properties of similar systems.

Measurements of decomposition voltages of systems composed of bromides of aluminum and copper, silver, antimony and bismuth, in different solvents with low dielectric constants (C_2H_5Br, C_6H_6, $C_6H_5CH_3$) [14], showed that, according to the value of the decomposition voltage, these metals are located in exactly the same series in solutions of these bromides, as in melts with aluminum bromide.

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* The temperature at which the measurements were carried out was much higher (250-300°) than for measurements in fused $AlBr_3$ (100°).

Measurements of individual electrode potentials carried out in benzene for a molar series corresponding to $AlBr_3 : C_6H_6 = 0.25$ and for a molar ratio of the corresponding bromide to aluminum bromide equal to 0.2-0.3 [15], gave a basis for placing the metals in such a series: Tl, Al, Cu, Ag, Bi, Sb.

V. S. Galinker [16], studied the electrode potentials of metals in solutions of $AlBr_3 - MeX^*$ – toluene for molar ratios $AlBr_3 : C_6H_5CH_3 = 0.25$ and a molar ratio of the corresponding metal bromide to $AlBr_3$ equal to 1.0, and obtained a voltage series (Al, Cu, Ag, Bi, Sb, As), which is no different from the voltage series for benzene solutions.

Examinations of voltage series in nonaqueous solutions and solvents with low dielectric constants show that they differ appreciably from the voltage series in aqueous solutions. Voltage series established for the solvents mentioned above differ very little among themselves, which explains the insignificant difference in one and the same electrolyte in these systems.

Delimarsky and colleagues who completed the greater part of the work on the investigation of transfer of metals in the voltage series, claim that the position of metals in a voltage series depends on the principles: "1) nature of the metal (ease of giving up electrons), 2) temperature, 3) complex formation in melts, 4) mutual polarization of atoms of the metal and anions" [17].

It is understood that the chemical activity of a metal is determined by the ease with which it gives up electrons and its place in the periodic system; hardly any exception can be taken to this, since it is not new; however, transfer of metals in a voltage series takes place and the chemical activity, in our opinion, forbids us to examine the principles of the transfer.

The question of the effect of "mutual polarization of atoms of the metal and anions" on the position of the metal in the voltage series has arisen comparatively recently,and therefore this factor has not received corresponding evaluation yet. As is known, interionic polarization in a given system, leads to strengthening of formation of complex compounds [18] and must have a similar effect on the magnitude of the electrode potential, however, Yu. K. Delimarsky [17], examining the mutual polarization of atoms of the metal (electrode) and anions, saying that this factor is a very substantial one, writes: "studying the effect of mutual polarization of the surface layer of atoms of the metal and anions of the fused salt, we must also keep in mind the role of temperature and the role of complex formation."

If such a type of polarization played any marked role at all, then, naturally, it would have to be taken into consideration in the magnitude of the emf of concentrated links of solutions and melts and there would have to be agreement between the theoretical amounts and the experimental data. Interaction between ions positively takes place therefore, and there is variation in the activity of the ions depending on the magnitude of the emf of concentrated bonds but here there is no "anion-atomic" polarization and therefore we assume that this factor should be dropped.

As we have pointed out already in the solutions examined above, the electrolytes are complex compounds of aluminum bromide with potential-determining ions in their outer zone. Therefore,mechanical transfer is explained directly for certain cases,but has no basis whatever for general application to transfer of metals in the voltage series. The bad effect of such a secondary issue on the effects under investigation is explained firstly by the fact that there was investigated, instead of searching for a definite linking and a definite dependence of the phenonema studied, one fact only – the transfer of metals in the voltage series – divorced from the residual effects, observed in the systems studied (in solutions). For this the newer attainments in science were ignored and all the efforts directed to facts relating to old ideas, although in the case of a number of factors, it is not suggested that complete perfection has been reached.

Actually, the nonaqueous solutions and melts examined above,in which the metals are arranged in some sort of voltage series, differ in properties from the aqueous solutions of the latter series,and this is not taken into account in the works quoted above.

In the first place, the molecular weight of the dissolved electrolytes in these media (solvents of low DC) is always greater than calculated according to their formulas [19]. In the second place the emf of concentrated links in solvents of low DC, as a rule, is always lower than calculated theoretically, when, as in concentrations

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* X = Halide.

Voltage Series of Metals for Their Bromides in Various Media

No.	Medium	Temperature	Concentration of bromide	Dielectric constants	Series															
1	$AlBr_3$ [9]	100°	—	3.37 [29]		Al		Zn	$Cd_{200°}$			$Ag_{120°}$			Hg			Sb	Bi	
2	$KBr—AlBr_3$ [10]	105	0.1N		Tl	Al		Zn	Cd		Sn	Ag	Cu	Fe.	Hg	Co*	Ni*	Sb	Bi	
3	$NaBr + 2AlBr_3$ [11] . . .	250—300	10 wt. %			Al		Zn	Cd	Pb	Sn	Ag	i	Cu	Hg					
4	$AlBr_3—C_6H_6$ [15]		$MeBr : AlBr_3 = 0.2$	2.23	Tl	Al						Cu	Ag					Bi	Sb	
5	$AlBr_3—C_6H_5CH_3$ [16] . .		$MeBr : AlBr_3 = 0.1$	2.29		Al						Cu	Ag					Bi	Sb	As
6	$NaBr—AlBr_3$ [23]	220—320	1 mole %			Al	Mn	Zn	Cd	Pb		Cu	Ag					Sb		
7	$NaBr \cdot AlBr_3$ [12]	260—500	5 mole %			Al	Mn	Zn	Cd	Pb	Sn	Cu	Ag	Fe	Hg	Co	Ni	Sb	Bi	
8	$ZnBr_2$ [24]	400				Al		Zn	Cd	Pb	Mn	Fe	Cu	Ag			Ni	Hg	Sn	Bi
9	$CdBr_2$ [25]	550	10 wt. %					Zn	Cd	Pb		Cu	Ag	Sn		Co	Ni		Bi	
10	Individual bromides [26]	700	100%		Mn	Al	Tl	Zn	Cd	Pb	Sn	Ag	Cu			Co			Bi	
11	H_2O [27]	25	—	81	Mg	Al	Mn	Zn	Cd	Tl	Co	Ni	Pb	Sn	Sb	Bi	Cu	Ag	Hg	

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* For Ni and Co bromides there are no data on the existence of complex compounds with $AlBr_3$.

of aqueous solutions, a satisfactory agreement is obtained [20]. In the third place, the molar electrical conductivity in these solvents is not increased with dilution as in aqueous solutions and falls. Curves of dependence of molar electrical conductivity on dilution frequently form maxima and minima.

The mutual linking of these effects was interpreted by us on the basis of a contemporary study of the structure of liquid substances [21]. According to the degree of dilution, beginning with an individual liquid electrode, the process of dilution of structural groups proceeds with formation of neutral ion pairs, the ions of which take part in transfer of current and "free" ions, i.e., the equilibrium lies between the "free" ions, neutral ion pairs and structural groups (associated). In the dependence on concentration, the ratio between the fractions indicated varies and this stipulates a variation in the properties studied. With variation in these properties, therefore, is linked the transfer of metals in the voltage series.

Some authors, examining the transfer of metals in the voltage series, indicate the role of the solvent but do not explain what this role includes; others refer to complex formation with the solvent [22].

We have already shown that such an explanation is correct only when the potential-determining ion displays complex formation, however, transfer of metals in the voltage series takes place when the potential-determining ion is   in the outer zone in the complex. Most of these series established for solutions in which the solvent is a dielectric with a low DC and in which there is complex formation, retain their basic order for the majority of metals in cases where the medium is a mixture of salts, and even for individual salts.

We compared the voltage series of metals, in the case of their bromides, for complexes, as well as for simple salts established by various methods in different media.

Series 1-5 (table) has been established for solutions in which the electrolytes were complex compounds of bromides of corresponding metals with aluminum bromide, since, for electrolytes of the first three series, $AlBr_3$ is regarded as the solvent, as this is located in the boundary and can enter into reaction with dissolved bromides. For electrolytes of series 4 and 5, the solvents were benzene and toluene and here the dissolved bromides form complex compounds with $AlBr_3$. On comparing these series, we see that there is very little variation between the substances themselves, only two pairs having exchanged places (Ag and Cu, Sb and Bi).

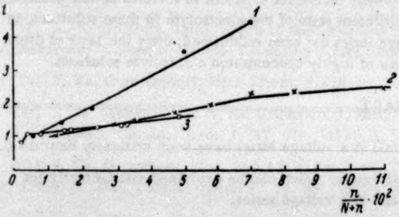
Transfer of bismuth and antimony is apparently linked with the different stabilities of the complexes $BiBr_3 \cdot AlBr_3$ and $SbBr_3 \cdot AlBr_3$. It is known that the complex compound $SbBr_3 \cdot AlBr_3$ in benzene solution, other conditions being the same, is less stable than $BiBr_3 \cdot AlBr_3$; therefore it may be said that in these five series, the arrangement of the metals is retained.

Of the known complex compounds of metal bromides with aluminum bromide, the most stable are complex compounds of $AlBr_3$ with bromides of alkali metals (compounds in the composition of which two or more molecules of one or another bromide may be fitted onto one molecule of $AlBr_3$, being hitherto unknown). Therefore, it may be said that the complex $NaBr \cdot AlBr_3$ is a medium which dissolves corresponding bromides and for this reason we take a mixture of electrolytes. There have been some series, obtained by two different methods (individual electrode potentials and dissociation pressure) for different electrolytes, which retain exactly the same order which they have in the first five series.

Let us compare now the series obtained for systems in which there are no complexes of aluminum bromide and no dielectric.

In these cases [8, 9], on comparing with series 10 for the individual bromides, manganese and copper have changed places, and tin has moved very noticeably. Comparing the series for individual bromides with the series 1-7, we find an insignificant variation in the position of the metals in these series.

From a comparison of the data, it follows that if there is transfer of metals in the voltage series, in cases with complex formation and potential-determining ions in these complexes which are in the inner zone, then the position of the metals in the series for systems in which the electrolytes are complex compounds of aluminum bromide would have to be suddenly changed from a series for individual bromides; this is not observed. Instead this confirms the statement above with reference to the view that transfer of metals in the voltage series cannot be explained in these cases by complex formation, because the potential-determining ion is in the outer zone. However, the position of metals in these series is very different from the series for aqueous solutions where the position is also controlled by concentration of potential-determining ions.



Dependence of degree of association of the electrolyte on concentration, in solvents of low DC.

1 — $BiBr_3 \cdot AlBr_3$—$AlBr_3$, 2 — $SbBr_3 \cdot AlBr_3$—$AlBr_3$,
3 —$HgBr_2 \cdot Al_2Br_6$—$AlBr_3$.

IV. How is the transfer of metals in the voltage series explained for those cases where the electrolyte is a complex in which the potential-determining ion is located in the outer zone ?

We have shown that what is called "anomalous" molar electrical conductivity is not an effect brought about by a definite group of solvents, and is the general rule for all highly concentrated electrolyte solutions [21, 28]. This rule is obeyed by solutions with decreasing concentration in solvents of low dielectric constant and highly concentrated solutions in solvents with low dielectric constants. This is explained by the fact that the solvent may not only enter into reaction with the dissolved substances to form corresponding complexes, but it depends on the molecular state of the electrolyte formed in the solution.

The lower the DC of the solvent, the greater the degree of association of the electrolyte. In other words, if we take one and the same concentration of any electrolyte in different solvents, with different DCs, then the degree of association of the electrolyte, other conditions being equal, will be greater in that solvent for which the dielectric constant is less.

The dependence of the degree of association of the electrolyte on concentration in solvents with a low DC, is seen from the figure, where the ordinate represents the degree of association of the electrolyte,and the abscissa the molar ratio $\frac{n}{N+n}$. As seen from the preceding figure, with increase in concentration of the electrolyte, its degree of association increases, since the highest degree of association for the three foregoing complexes occurs for the complex $BiBr_3 \cdot AlBr_3$ in aluminum bromide as solvent. This same rule applies to other solvents with low DC (C_6H_6, $C_2H_4Br_2$, etc.).

Ions which enter into the composition of structural groups are potential-determining, therefore in that field of concentration to which the law of highly concentrated solutions applies, the magnitude of the potential-determining ions may be measured not only owing to the fact that they are located in the complex in the inner zone, but, being located in the outer zone of a complex in a given field of concentration, are bound in structural groups in which they have not yet become potential-determining, i.e., they also play the same part in those complexes where they are coordinated. Consequently, in the solutions examined, free ions in melts must be potential-determining. That is, variations in their concentration are controlled by the potential of some metal or other and by its place in the voltage series. Formation of structural groups depends on the concentration of the electrolyte, the magnitude of the dielectric constant of the solvent and the nature of both anion and cation. Interaction forces, apparently present here, are the same as for the ionic lattice.

Thus, observed variations in different properties in the solutions examined and the transfer of metals in the voltage series are in agreement. In conjunction with this we have shown how the effect of association of the electrolyte, with increase in its concentration, and decrease in molecular electrical conductivity with dilution, as well as transfer of metals in the voltage series, is linked with the molar state of the electrolyte in solution.

A sudden alteration in the position of metals in the voltage series, for solutions in solvents of low dielectric constant in the aqueous solution series, is linked with the different state of the electrolyte in these solutions, in that aqueous solutions, for concentrations for which a voltage series has been established, obey the laws of dilute solutions, as solutions in solvents with low DC obey the law of highly concentrated electrolyte solutions.

SUMMARY

1. Existing views on the principles of transfer of metals in a voltage series have been critically examined.

2. It has been shown to be erroneous that mechanical transfer which can be explained satisfactorily for certain cases, can be applied to all cases of transfer of metals in a voltage series.

3. It has been shown that any complex formation must lead to transfer of metals in a voltage series. It is necessary to consider the zone in which potential-determining ions exist and the stability of the complex.

4. A connection has been shown between the effects of association (stages of regularity) of the electrolyte and increase in its concentration, decreased viscosity correction, molar electrical conductivity on dilution and transfer of metals in a voltage series.

5. An interpretation is given of the transfer of metals in the voltage series based on a corresponding study of the structure of a liquid substance.

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DETERMINATION OF SOLUBILITY OF SPARINGLY SOLUBLE COMPOUNDS WITH THE AID OF ANISOTROPIC RADIOACTIVE INDICATORS

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Many methods are known for determining solubility of sparingly soluble compounds, with varying degrees of accuracy. The most widespread are represented by physicochemical methods. It should, however, be mentioned that, apart from their merits, these methods have some disadvantages, the main one being that in practice sometimes the solubility can only be determined in a pure solvent (water) in absence of extraneous ions.

The use of radioactive indicators increases the possibility of investigations in many fields of chemistry, among them being determinations of solubility. The simplicity of the method, use of small amounts of material, and particularly the possibility of determining the solubility not only in pure water, but in solutions of different electrolytes, confirms the expediency of using radioactive indicators in these studies.

Radiometric methods are described in the literature for determining solubility with the use of natural or synthetic radioactive indicators [1-13]. In these, in all cases the radioactive indicators comprise isotopes of one of the elements entering into the composition of the sparingly soluble compounds under investigation. Thus, the solubility may only be determined of those substances which contain elements which are satisfactory for determination of radioactive isotopes (a sufficiency of radiation energy suitable for work in a partly decayed state, the possibility of obtaining a preparation with a high specific activity, etc.). In the absence of such isotopes, radioactive determination of solubility is difficult or impossible.

A method is proposed by us for radioactive determination of solubility in absence of isotopes of elements suitable for the work, which enter into the composition of the compound under investigation. In such cases the radioactive isotope of another element, particularly an isomorphous one, which enters into the crystal lattice of the compound under test, may be used as an indicator.

Isomorphous, anisotropic radioactive additions have already been used for some chemical investigations. There may be mentioned determination of calcium in the form of oxalate, where the calcium content is estimated according to the amount of isomorphous thorium B precipitated [14]. We may mention also the investigation of the distribution of barium between lead nitrate and its saturated solution, carried out by using radium as indicator [15]. For indicating zirconium, the radioactive isotope of hafnium has been used [16]. Anisotropic indicators have also been found useful for determining the magnitude of the surface of solid substances [17].

We studied the use of anisotropic indicators for determining the solubility of sparingly soluble compounds at room temperature. With this object in view, we carried out solubility determinations of mercury tetrathiocyanate of composition $Me[Hg(CNS)_4]$, where Me is Zn, Cd, Cu.

The formation of mixed crystals in this group of compounds is well known and has often been used in practical chemical investigations [18-27]. We suggested that mercury tetrathiocyanate may be used for deciding the problem before us. Solubility was studied of

$$Zn[Hg(CNS)_4], \quad Cd[Hg(CNS)_4] \text{ and } Cu[Hg(CNS)_4]$$

using anisotropic indicators of the corresponding radioactive additions. First, the solubility of $Me[Hg(CNS)_4]$ was studied using radioactive cobalt (Co^{60}) as indicator.

For this, we added a definite amount of radioactive microcomponent ($3\ \gamma$/ml cobalt labeled with the radioactive isotope Co^{60}), to a solution of the macrocomponent of known concentration (2 mg $Zn^{\cdot\cdot}$, 4 mg $Cd^{\cdot\cdot}$ or $Cu^{\cdot\cdot}$ per ml), determined the radioactivity of the solution formed and calculated the activity (in imp /min) for 1 mg macrocomponent (specific activity). A large excess of precipitant – potassium mercurytetrathiocyanate* was introduced into the solution. Under such conditions the macrocomponent is precipitated almost completely, and with sufficiently good mixing, practically complete precipitation of the macrocomponent leads to a practically complete precipitation of the microcomponent [28]. It follows that the ratio of the amount of micro- and macrocomponent in the precipitate and its specific activity must be practically the same as for the original solution.

From the washed precipitate a saturated solution was prepared, from the activity of which the solubility was calculated. For this, it was assumed that saturation is reached very much more quickly than the thermodynamic equilibrium between the macro- and microcomponents and that in the saturated solution obtained, the ratio indicated does not vary. These assumptions were confirmed experimentally by us for the example of the mixed crystals $(Cd, Co)[Hg(CNS)_4]$.

A mixture was prepared of solutions of nitrates of cadmium (4 mg $Cd^{\cdot\cdot}$/ml) and cobalt ($3\ \gamma\ Co^{\cdot\cdot}$/ml) containing the isotopes Cd^{115} and Co^{60} as radioactive indicators. Thus, two radioactive indicators were located in the mixture. The method of determining two radioactive elements in admixture given in the literature [29], permits the calculation of the ratio of the activity of the given components and subsequently the study of the ratio of concentration of cobalt and cadmium in the original and the saturated solutions as well as in the precipitate $(Cd, Co)[Hg(CNS)_4]$.

The investigations showed that within the limits of error of the test these ratios remain constant. This shows the main possibility for determining the solubility of sparingly soluble compounds according to their isomorphous anisotropic additions.

According to the method described above, saturated solutions were obtained of sparingly soluble mercury tetrathiocyanates. The solubility was calculated (in moles/liter) according to the formula:

$$\frac{A_x}{A_{sp}\cdot g} = s,$$

where A_x is the activity of 1 ml of saturated solution (imp /min), $A_{sp.}$ is the specific activity (imp /min) for 1 mg cation of macrocomponent, g is the atomic weight of the macrocomponent.

The specific activity lay within the limits 2500-3200 imp /min for 1 g cation. The solubility of the mercury tetrathiocyanates was determined for various ratios of the amount of micro- and macrocomponents. The results of the investigations are given in Table 1, where the data for 4-6 parallel determinations are given.

Comparisons of the solubility values determined using radioactive isotopes of zinc and cadmium with the solubility figures found from radioactive isomorphous addition of cobalt, confirms the possibility of determining solubility according to anisotropic addition with sufficient accuracy. We determined the solubility of $Cu[Hg(CNS)_4]$ using this method. Direct determination of the solubility using the radioactive isotope of copper is possible under ordinary laboratory conditions since all radioactive isotopes of copper are characterized by very small half-lives, and the measurements must be carried out hourly and also in minutes and seconds [30].

We also studied the possibility of determining solubility using other anisotropic isomorphous indicators. Thus, for determining the solubility of zinc and copper mercurytetrathiocyanates, Cd^{115} was used as an isomorphous admixture, and in the case of cadmium mercurytetrathiocyanate – Zn^{65} (Table 2).

Absolute values of the solubility found by us, by various methods, agree satisfactorily with each other and in some cases the variation of the maximum was tested 2-3 times. These variations may be explained by experimental errors and also by disturbance of the ratio of the amounts of the components in the original and in the final saturation solution.

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* For preparing the reagent we dissolved 15.8 g $Hg(CNS)_2$ and 9.7 g KCNS in 100 ml water.

TABLE 1

$Me[Hg(CNS)_4]$	Indicator	Ratio $Co^{\cdot\cdot} : Me^{\cdot\cdot}$	Solubility (mole/liter)	
$Zn[Hg(CNS)_4]$	Zn^{65}	—	$4.5 \cdot 10^{-4}$	$4.7 \pm 0.4 \cdot 10^{-4}$
			$5.2 \cdot 10^{-4}$	
			$4.8 \cdot 10^{-4}$	
			$5.2 \cdot 10^{-4}$	
			$4.2 \cdot 10^{-4}$	
			$4.6 \cdot 10^{-4}$	
	Co^{60}	1 : 725	$4.5 \cdot 10^{-4}$	
			$4.3 \cdot 10^{-4}$	$4.6 \pm 0.2 \cdot 10^{-4}$
			$4.6 \cdot 10^{-4}$	
			$4.5 \cdot 10^{-4}$	
			$4.6 \cdot 10^{-4}$	
	Co^{60}	1 : 1660	$5.3 \cdot 10^{-4}$	$5.4 \pm 0.4 \cdot 10^{-4}$
			$5.9 \cdot 10^{-4}$	
			$5.2 \cdot 10^{-4}$	
			$4.8 \cdot 10^{-4}$	
			$5.3 \cdot 10^{-4}$	
			$5.8 \cdot 10^{-4}$	
	Co^{60}	1 : 2100		$4.5 \cdot 10^{-4}$
$Cd[Hg(CNS)_4]$	Cd^{115}	—	$4.5 \cdot 10^{-3}$	
			$4.2 \cdot 10^{-3}$	$4.0 \pm 0.5 \cdot 10^{-3}$
			$3.7 \cdot 10^{-3}$	
			$3.4 \cdot 10^{-3}$	
			$4.8 \cdot 10^{-3}$	
			$3.5 \cdot 10^{-3}$	
	Co^{60}	1 : 1330	$3.4 \cdot 10^{-3}$	$3.2 \pm 0.2 \cdot 10^{-3}$
			$3.0 \cdot 10^{-3}$	
			$3.1 \cdot 10^{-3}$	
			$3.4 \cdot 10^{-3}$	
			$3.1 \cdot 10^{-3}$	
			$3.2 \cdot 10^{-3}$	
	Co^{60}	1 : 2660	$3.4 \cdot 10^{-3}$	$3.5 \pm 0.3 \cdot 10^{-3}$
			$3.8 \cdot 10^{-3}$	
			$3.6 \cdot 10^{-3}$	
			$3.2 \cdot 10^{-3}$	
			$3.8 \cdot 10^{-3}$	
$Cu[Hg(CNS)_4]$	Co^{60}	1 : 1330	$7.4 \cdot 10^{-4}$	$8.6 \pm 1.1 \cdot 10^{-4}$
			$9.5 \cdot 10^{-4}$	
			$9.0 \cdot 10^{-4}$	

TABLE 2
Determination of Solubility of $Md[Hg(CNS)_4]$ Using Anisotropic Isomorphous Indicators.

Indicator	Solubility (in mole/liter)		
	$Zn[Hg(CNS)_4]$	$Cd[Hg(CNS)_4]$	$Cu[Hg(CNS)_4]$
$Me^{\cdot\cdot}$	$4.7 \pm 0.4 \cdot 10^{-4}$	$4.0 \pm 0.5 \cdot 10^{-3}$	—
Co^{60}	$4.9 \pm 0.4 \cdot 10^{-4}$	$3.3 \pm 0.3 \cdot 10^{-3}$	$8.6 \pm 1.1 \cdot 10^{-4}$
Zn^{65}	—	$1.1 \pm 0.1 \cdot 10^{-3}$	—
Cd^{115}	$6.7 \pm 0.3 \cdot 10^{-4}$	—	$4.4 \pm 0.4 \cdot 10^{-4}$

We assume that the method of anisotropic indicators extends slightly the possibility of determining the solubility of sparingly soluble compounds by the radioactive method. However, some limitations must be pointed out. The method of anisotropic indicators may only be used for determining solubility under the following conditions:

1. The radioactive anisotropic indicator must enter isomorphously into the crystal lattice of the sparingly soluble compound under investigation.

2. The amount of anisotropic indicator must be very small and form such a small portion that the solubility of mixed crystals formed does not differ practically from the solubility of the pure crystals of the compound investigated. In this case the possibility is also decreased of exchange between the microcomponents situated in the saturated solution and the precipitate.

3. In connection with the latter it is desirable to use radioactive preparations of high specific activity.

SUMMARY

1. The possibility is demonstrated of determining solubility of sparingly soluble compounds using anisotropic isomorphous indicators.

2. The method is used for determining solubility of zinc, cadmium and copper mercurytetrathiocyanates.

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ADIAGONAL RECIPROCAL SYSTEM OF CHLORIDES AND TUNGSTATES OF SODIUM AND POTASSIUM

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In the present work the results are given of an investigation of the system Na, K ‖ Cl, WO_4, on two adjacent lateral sides of which there is complex formation. Thus, sodium chloride forms a compound of composition $Na_2Cl_2 \cdot 2Na_2WO_4$ with sodium tungstate, which melts without decomposition. In the binary system of tungstates of sodium and potassium, two compounds are formed which melt with decomposition, the composition of which, apparently, is as follows: $2\,Na_2WO_4 \cdot K_2WO_4$ and $Na_2WO_4 \cdot K_2WO_4$.

Thus, the chemical nature of the system Na, K ‖ Cl, WO_4, has been determined on the basis of the existence of complex formation in lateral binary systems.

EXPERIMENTAL

Method. The investigations were carried out by the visual polythermal method. The melts, in a platinum dish, were stirred vigorously with a platinum stirrer until the whole slowly cooled down and crystals appeared in the melt; these were watched until they disappeared. The initial chlorides, chemically pure grade, were recrystallized; tungstates of sodium and potassium were prepared by melting the carbonates (c. p. grade) and freshly prepared tungstic anhydride with subsequent recrystallization. M. p. NaCl 800°, KCl 775°, Na_2WO_4 698°, K_2WO_4 926°.

All the compositions refer to gram-equivalent percents.

The complex compounds formed in the system are designated in the figures and tables as follows: $D_I - 2Na_2WO_4 \cdot Na_2Cl_2$; $D_{II} - 2Na_2WO_4 \cdot K_2WO_4$; $D_{III} - Na_2WO_4 \cdot K_2WO_4$.

TABLE 1

Na_2WO_4—K_2WO_4				Na_2WO_4—Na_2Cl_2		K_2WO_4—K_2Cl_2		Na_2WO_4—K_2Cl_2	
% K_2WO_4	Temperature	% K_2WO_4	Temperature	% Na_2Cl_2	Temperature	% K_2Cl_2	Temperature	% K_2Cl_2	Temperature
0	698°	55	744°	0	698°	0	926°	0	698°
5	677	60	770	5	666	5	898	5	658
10	658	65	790	10	644	10	872	7.5	640
12.5	654	70	810	13	644	15	836	10	616
15	645	75	834	16	652	20	804	15	606
17.5	645	80	853	19	660	25	772	17.5	605
20	645	82.5	860	25	670	30	740	20	600
22.5	645	85	866	28	675	35	700	25	592
25	654	87.5	882	34	680	38	685	35	564
30	662	90	894	37	680	41	664	40	540
35	670	97.5	916	43	672	44	646	42.5	530
37.5	674	100	926	46	666	47	643	45	526
40.0	676	—	—	49	670	50	660	50	564
42.5	686	—	—	52	682	53	670	52.5	578
45	698	—	—	58	704	59	680	57.5	601
50	722	—	—	100	800	100	775	100	775

TABLE 2

Section II		Section XVII		Section I		Section IV		Section VII	
17% K_2WO_4 $\rightarrow Na_2Cl_2$ 83% Na_2WO_4		93% Na_2WO_4 $\rightarrow K_2WO_4$ 7% Na_2Cl_2		94% Na_2WO_4 $\rightarrow Na_2Cl_2$ 6% K_2WO_4		73% Na_2WO_4 $\rightarrow Na_2Cl_2$ 27% K_2WO_4		16% Na_2WO_4 $\rightarrow Na_2Cl_2$ 84% K_2WO_4	
% Na_2Cl_2	Temperature	% K_2WO_4	Temperature	% Na_2Cl_2	Temperature	% Na_2Cl_2	Temperature	% Na_2Cl_2	Temperature
0	645°	0	658°	0	676°	0	660°	0	869°
5	606	5	648	5	650	2.5	654	32.5	564
10	598	8	640	7.5	638	5	645	35	550
12.5	605	11	628	10	620	7.5	626	37.5	532
15	601	13	620	12.5	625	10	613	40	518
17.5	618	15	620	15	636	12.5	598	42.5	530
20	626	17	620	17.5	644	15	586	45	532
25	636	19	620	20	652	17.5	590	47.5	540
30	640	21	626	—	—	20	598	50	546
35	646	23	632	—	—	22.5	604	52	552
45	654	25	636	—	—	25	606	54	557
47.5	651	34	646	—	—	30	622	56	560
50	656	37	656	—	—	35	631	58	576
55	672	40	666	—	—	—	—	60	596
60	690	43	677	—	—	—	—	—	—
65	706	49	700	—	—	—	—	—	—

Binary Systems

1. $Na_2Cl_2-K_2Cl_2$ represents a specific system with a continuous series of solid solutions with a minimum at 660° [1] (Fig. 1). The solid solutions begin to decompose below 500°.

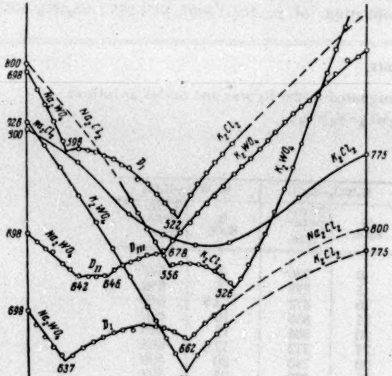


Fig. 1. Binary laterals and diagonal sections of the system Na, K ‖ Cl, WO_4.

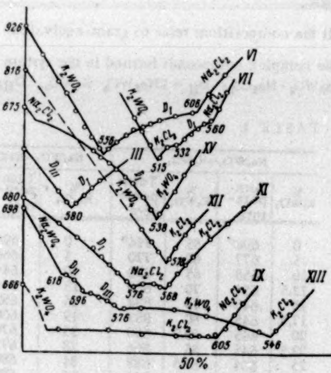


Fig. 2. Internal sections of the system.

TABLE 2 (continued)

Section IX		Section XVI		Section XI		Section XII		Section V	
60% K_2WO_4 $\rightarrow Na_2Cl_2$ 40% K_2Cl_2		33% Na_2Cl_2 $\rightarrow K_2WO_4$ 67% Na_2WO_4		33% Na_2Cl_2 $\rightarrow K_2Cl_2$ 67% Na_2WO_4		45% K_2WO_4 $\rightarrow Na_2WO_4$ 55% K_2Cl_2		33% K_2WO_4 $\rightarrow Na_2Cl_2$ 67% Na_2WO_4	
% Na_2Cl_2	Temperature	% K_2WO_4	Temperature	% K_2Cl_2	Temperature	% Na_2WO_4	Temperature	% Na_2Cl_2	Temperature
0	666°	0	680°	0	680°	0	664°	0	666°
25	612	15	625	10	648	20	572	6	633
35	604	20	608	15	632	25	551	10	608
45	604	25	594	20	618	30	550	12.5	593
50	604	30	577	25	598	35	555	15	574
52.5	604	35	566	30	579	45	578	17.5	567
55	604	40	585	35	576	55	576	20	586
57.5	606	45	606	37.5	575	65	576	22.5	594
60	614	50	627	40.0	572	70	575	25	598
62.5	630	—	—	42.5	575	72.5	580	30	608
65	644	—	—	45	588	77.5	591	35	618
—	—	—	—	50	606	80	596	40	620
—	—	—	—	55	630	82.5	600	45	620
—	—	—	—	60	648	85	612	50	622
—	—	—	—	—	—	87.5	616	60	670
—	—	—	—	—	—				

2. $Na_2Cl_2-Na_2WO_4$ was investigated by us. A compound composition $2Na_2WO_4 \cdot Na_2Cl_2$ is formed, melting without decomposition at 680°. Eutectic points: 637° and 10.5% Na_2Cl_2, 622° and 47.5% Na_2Cl_2, (Fig. 1, Table 1).

3. $Na_2WO_4-K_2WO_4$. Course of crystallization corresponds to solid solutions which are decomposed in the solid state with formation of a compound composition 1:1 [2]. This compound melts with decomposition at 689° and 55% Na_2WO_4 [3]. In the range from 79 to 86% Na_2WO_4 there is decomposition, possibly corresponding to the other compound. According to our data (Fig. 1, Table 1), two compounds are formed in the system, apparently of composition $2Na_2WO_4 \cdot K_2WO_4$ and $Na_2WO_4 \cdot K_2WO_4$, melting with decomposition at 646° and 23.5% K_2WO_4, at 678° and 40% K_2WO_4, respectively. The eutectic corresponds to 642° and 15.5% K_2WO_4.

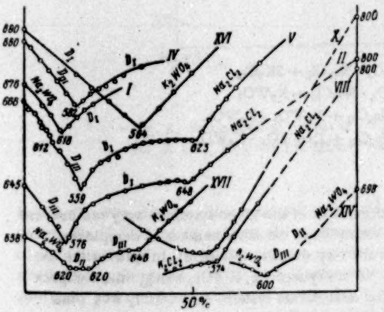


Fig. 3. Internal sections of the system.

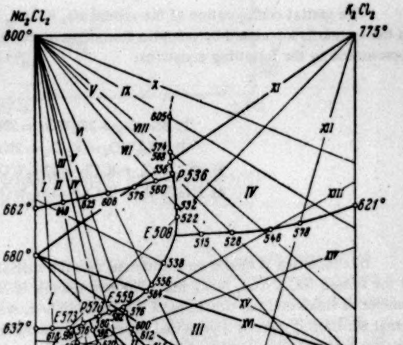

Na_2Cl_2
K_2Cl_2
800°
775°
662°
680°
637°
698°
621°
926°
642°
646°
678°
Na_2WO_4
K_2WO_4
P536
E508
E559
P570
E573
IV
III
I
II
V
IX
X
XI
XII
XIII
XIV
XV
XVI
XVII
VI
VII
VIII
605
579
568
556
560
576
606
625
648
532
522
515
528
548
578
538
556
564
576
600
612
646
620

Fig. 4. Distribution of sections and triangulation of the system.

4. $K_2Cl_2-K_2WO_4$. According to data in the literature, the eutectic decomposition point is at 621° and 47% K_2Cl_2 [4]. Our data do not differ from the data of the authors indicated above. The eutectic corresponds to 621° and 47% K_2Cl_2.

The reciprocal system Na, K ‖ Cl, WO_4. 19 internal sections through the system were investigated, 2 of which were diagonal (Figs. 1-3). Data for the most characteristic of the sections are given in Table 2.

The surface of crystallization of the system consists of the following fields: sodium tungstate, potassium tungstate, solid solutions of chlorides of sodium and potassium, the complexes $2Na_2WO_4 \cdot Na_2Cl_2$, $2Na_2WO_4 \cdot K_2WO_4$ and the field $Na_2WO_4 \cdot K_2WO_4$. The field of the complex $2Na_2WO_4 \cdot Na_2Cl_2$ enters right into the system, and its composition point is represented by an area of quaternary triangular stars. (Figs. 4, 5).

The reciprocal system of the four triangular sections: $D_I - K_2Cl_2$, $D_I - K_2WO_4$, $D_I - D_{III}'$, $D_I - D_{II}$ is divided into 5 phase triangles: I) $D_I - Na_2Cl_2 - K_2Cl_2$; II) $D_I - K_2Cl_2 - K_2WO_4$; III) $D_I - K_2WO_4 - D_{III}$; IV) $D_I - D_{III} - D_{II}$; V) $D_I - D_{II} - Na_2WO_4$. The phase tree of the crystallization system consists of 5 nonvarying points, 3 of which are eutectics and 2 transition points. Composition and temperature of the nonvarying points are given in Table 3.

TABLE 3

Character of points	Temperature	Composition (in %)			Equilibrium phases
		Na_2Cl_2	Na_2WO_4	K_2WO_4	
Transition P_V	536°	56	1	43	D_I, K_2Cl_2, Na_2Cl_2
Eutectic E_{IV}	508	38.5	18	43.5	D_I, K_2Cl_2, K_2WO_4
Eutectic E_{III}	559	17	55	27.5	D_I, K_2WO_4, D_{III}
Transition P_{II}	578	13	70	17	D_I, D_{III}, D_{II}
Eutectic E_I	573	11	77	12	D_I, DI_I, Na_2WO_4

In Fig. 6 a projection is shown of the course of mutual crystallization on the plane of the polytherm of the binary system $Na_2WO_4-K_2WO_4$.

The spatial configuration of the system Na, K ‖ Cl, WO_4 and its triangles shows that the exchange reaction in the system is suppressed by complex formation reactions. The chemical relationship in the system may be represented by the following equations:

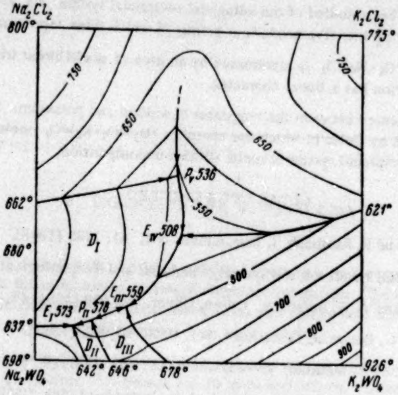
$$1)\ 3Na_2Cl_2 + 2K_2WO_4 = 2Na_2WO_4 \cdot Na_2Cl_2 + 2K_2Cl_2,$$

$$2)\ 3Na_2WO_4 + K_2Cl_2 = 2Na_2WO_4 \cdot Na_2Cl_2 + K_2WO_4,$$

$$3)\ 4Na_2WO_4 + K_2Cl_2 = 2Na_2WO_4 \cdot Na_2Cl_2 + NaWO_4 \cdot K_2WO_4,$$

$$4)\ 5Na_2WO_4 + K_2Cl_2 = 2Na_2WO_4 \cdot Na_2Cl_2 + 2Na_2WO_4 \cdot K_2WO_4.$$

In conclusion it should be mentioned that the spatial configuration of the given system is very reminiscent of the system Na, K ‖ Cl, MoO_4 [5]. The two laterals of both systems have the same number of complexes. The number of fields and the character of the fields in both systems are very similar. However, in spite of the external similarity, there is a principal difference between them. In the system Na, K ‖ Cl, MoO_4, the complex $Na_2Cl_2 \cdot Na_2MoO_4$ is represented by an area of trilinear triangular stars; in the system Na, K ‖ Cl, WO_4 the



Na_2Cl_2
800°
K_2Cl_2
775°
750
750
650
650
650
P_I 536
550
662°
621°
E_{IV} 508
D_I
680°
E_{III} 559
E_I 573
P_{II} 578
600
700
837°
800
900
D_{II}
D_{III}
698°
Na_2WO_4
642°
646°
678°
926°
K_2WO_4

Fig. 5. Projection of surface of crystallization of the system Na, K ‖Cl, WO_4 on the composition square.

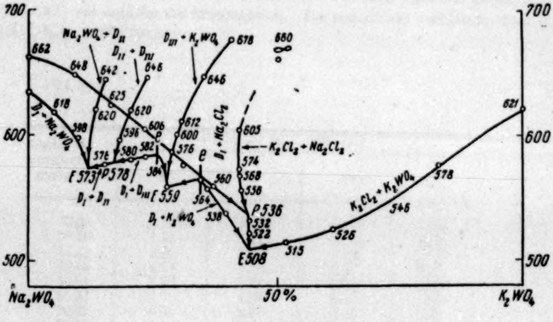


Fig. 6. Projection of curves of mutual crystallization of the reciprocal system Na, K ‖Cl, WO_4 on the lateral $Na_2WO_4 \cdot K_2WO_4$.

$Na_2Cl_2 \cdot Na_2WO_4$ complex is represented by a field of quatrilinear triangular stars. The eutectic tree of the system Na, K ‖Cl, MoO_4 consists of five nonvarying points having the form of a branched tree with a closed triple eutectic point not linked with the nonvarying points of the lateral binary systems. The tree of the crystallization system Na, K ‖Cl, WO_4 is represented by open linear stretches. Such systems having external similarity and the same number of geometric elements, according to the different views on triangulation and consequently chemism, were named "topological isomers" by N. S. Kurnakov [6].

SUMMARY

1. Fusion diagrams have been studied of the adiagonal reciprocal system $\mathrm{Na, K \parallel Cl, WO_4}$ consisting of six fields of crystallization split up into five nonvariant points, of which three represent eutectics.

2. The compound $\mathrm{2Na_2WO_4 \cdot Na_2Cl_2}$ is represented by an area of quadrilinear triangular stars as a result of which the tree of crystallization has a linear character.

3. The two complexes formed between the tungstates of sodium and potassium in the given system represent substances characterized by fields in which the complex $\mathrm{Na_2WO_4 \cdot K_2WO_4}$ melts with decomposition in the binary system; inside the reciprocal system it melts without decomposition.

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* T. p. = C. B. Translation pagination.

THE STANNIC CHLORIDE – PHENOL SYSTEM

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The literature contains descriptions of a large number of complex compounds formed by stannic chloride with substances belonging to the most varied classes of chemical compounds. The most stable crystalline compounds are formed by stannic chloride and typical bases. This fact agrees well with the idea that reactions involving complex formation may be regarded as acid-base reactions [1].

It seemed of interest to us to follow the connection between complex formation and acid-base reaction in the systems formed by stannic chloride with phenol and its nitro derivatives. In the present work the results are given of a study of the system stannic chloride – phenol. Data will be given in later communications on systems formed by stannic chloride and certain phenol derivatives.

EXPERIMENTAL

The preparation and purification of the stannic chloride have been described earlier [2]. Stannic chloride with b. p. 110.5° (705 mm) was used for the investigation. The phenol was purified by three distillations, after which it had m. p. 41°, b. p. 176° (700.3 mm).

TABLE 1

C_6H_5OH content (mole %)	Viscosity in centipoises			
	20°	40°	60°	80°
0.00	0.927	0.758	0.637	0.540
30.20	1.82	1.21	0.864	0.651
41.22	2.80	1.63	1.08	0.767
49.46	4.17	2.19	1.38	0.937
56.61	5.97	2.73	1.55	1.03
66.37	11.9	4.28	2.11	1.26
70.32	16.3	4.97	2.29	1.33
72.58	21.6	5.56	2.41	1.36
76.06	25.9	6.28	2.57	1.40
79.83	38.4	7.92	2.96	1.58
84.51	47.4	8.64	3.15	1.64
89.94	42.7	8.65	3.26	1.70
90.39	40.4	8.54	3.27	1.73
100.00	—	4.79	2.48	1.52

No noticeable thermal effect was observed when the stannic chloride was added to the phenol. When the colorless components were mixed, a yellow-colored solution was obtained.

The viscosity, density and electrical conductivity of the solutions were measured at 20, 40, 60 and 80°, and the vapor pressure measured at 40, 60 and 80°.

The results of the viscosity measurements are given in Table 1 and pictured graphically in Figs. 1 and 2.

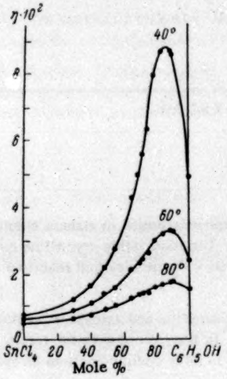

Fig. 1. Relationship between viscosity and composition.

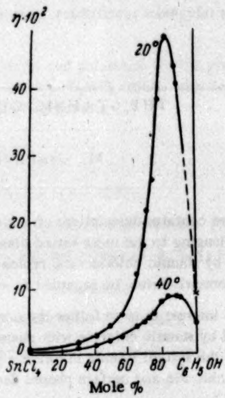

Fig. 2. Relationship between viscosity and composition.

The viscosity isotherms (Figs. 1 and 2) pass through a maximum. The viscosity at 20° is so great that it cannot be conveniently shown on the same diagram as the viscosities at the higher temperatures. In Fig. 2, therefore, we have shown the isotherm corresponding to 20° together with one other isotherm (40°). With increase in temperature the maximum on the viscosity curves moves in the direction of the more viscous component – the phenol: at 20° the viscosity maximum lies approximately at 85-87 mole % C_6H_5OH, while at 80° it lies at 90 mole % C_6H_5OH.

TABLE 2

C_6H_5OH content (mole %)	20°		C_6H_5OH content (mole %)	40°		C_6H_5OH content (mole %)	60°		C_6H_5OH content (mole %)	80°	
	$\kappa \cdot 10^5$	$\kappa \cdot \eta \cdot 10^5$		$\kappa \cdot 10^5$	$\kappa \cdot \eta \cdot 10^5$		$\kappa \cdot 10^5$	$\kappa \cdot \eta \cdot 10^5$		$\kappa \cdot 10^5$	$\kappa \cdot \eta \cdot 10^5$
41.22	0.57	0.0159	42.53	0.611	0.0107	58.33	1.92	0.0319	42.74	0.294	0.00230
48.00	1.28	0.0493	49.87	1.29	0.0279	66.92	3.42	0.0718	61.69	1.75	0.0201
55.46	1.87	0.113	57.86	2.57	0.0758	73.24	4.69	0.120	76.98	3.41	0.0504
61.98	2.49	0.224	71.45	4.81	0.249	79.21	5.56	0.167	81.53	3.60	0.0571
67.84	2.93	0.395	72.90	5.39	0.300	84.86	5.79	0.187	85.51	3.39	0.0565
72.01	3.04	0.578	75.61	5.76	0.360	87.66	5,36	0.175			
75.02	2.94	0.703	77.20	6.00	0.408	90.53	4.64	0.153			
80.30	2.59	1.04	79.20	6.12	0.474	93.35	3.55	0.113			
83.60	2.50	1.18	80.81	6.15	0.505	95.81	2.31	0.0705			
85.78	2.45	1.16	83.93	6.01	0.517	97.50	1.43	0.0409			
87.78	2.44	1.02	85.47	5.90	0.512	98.06	0.991	0.0279			
87.90	2.39	1.10	87.26	5.65	0.493						
90.51	2.25	0.909									
91.41	2.29	0.857									

A mixture of stannic chloride and phenol shows an electrical conductivity of the order of 10^{-5} ohm^{-1} cm^{-1}. The results of the electrical conductivity measurement are given in Table 2. Here also are given values for the corrected electrical conductivity ($\kappa \cdot \eta$).

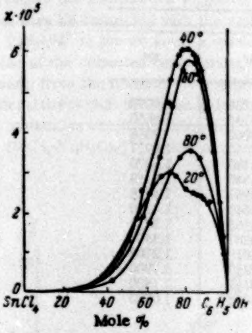

Fig. 3. Relationship between specific conductivity and composition.

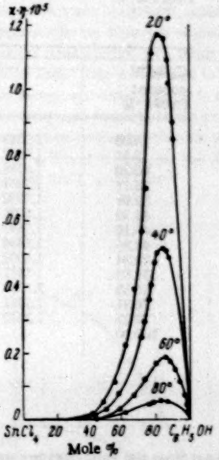

Fig. 4. Relationship between corrected electrical conductivity and composition.

The specific conductivity isotherms (Fig. 3) pass through a maximum in the region 70-85 mole % C_6H_5OH, and with increasing temperature this maximum is displaced first toward the phenol side and then, at temperatures above 60°, toward the stannic chloride side. The isotherm for the specific conductivity at 20° shows an inflection in the region 81-82 mole % C_6H_5OH. The corrected electrical conductivity isotherms (Fig. 4) at all temperatures take the form of smooth curves passing through a maximum which does not shift with changing temperature. The maximum lies in the region 84-85 mole % C_6H_5OH. The corrected electrical conductivity falls rapidly with increase in temperature. The values of the temperature coefficient of the corrected electrical conductivity are given in Table 3.

TABLE 3

C_6H_5OH content (mole %)	Temperature coefficient of the corrected electrical conductivity (%)				
	20–40°	20–60°	20–80°	40–60°	40–80°
50.0	−2.6	−2.0	−1.5	−3.0	−1.9
55.0	−2.4	−2.0	−1.5	−2.9	−2.0
60.0	−2.4	−2.0	−1.5	−3.0	−2.0
65.0	−2.5	−2.0	−1.5	−3.1	−2.1
70.0	−2.6	−2.0	−1.5	−3.0	−2.1
75.0	−2.5	−2.1	−1.6	−3.1	−2.2
80.0	−2.8	−2.1	−1.6	−3.2	−2.2
85.0	−2.8	−2.1	−1.6	−3.2	−2.2
90.0	−2.6	−2.1	−1.6	−3.2	−2.2
95.0	−2.4	−2.1	−1.5	−3.3	−2.2

The temperature coefficient of the corrected electrical conductivity does not depend on the composition.

The density determination results are given in Table 4. The specific volume isotherms (Fig. 5) indicate that a contraction takes place in the system.

TABLE 4

C_6H_5OH content (mole %)	Density			
	20°	40°	60°	80°
0.00	2.2340	2.1819	2.1288	2.0790
13.41	1.9882	1.9447	1.8986	1.8650
20.20	1.8788	1.8354	1.8060	1.7618
26.11	1.7967	1.7711	1.7256	1.6927
32.01	1.7250	1.6633	1.6480	1.6070
41.59	1.6076	1.5879	1.5540	1.5159
46.10	1.5697	1.5320	1.4951	1.4745
48.85	1.5346	1.4954	1.4640	1.4340
52.84	1.4902	1.4552	1.4165	1.3822
58.83	1.4411	1.4117	1.3802	1.3407
66.33	1.3679	1.3302	1.3018	1.2708
76.31	1.2761	1.2433	1.2239	1.1900
77.22	1.2672	1.2391	1.2151	1.1800
100.00	—	1.0601	1.0443	1.0230

It turned out from the vapor-pressure measurements that the total vapor pressure in our experiments was identical with the partial vapor pressure of the stannic chloride. The absence of phenol in the distillate was established by the qualitative test with $FeCl_3$. The vapor-pressure measurement results are given in Table 5.

TABLE 5

C_6H_5OH content (mole %)	Vapor pressure (mm Hg)		
	40°	60°	80°
0.00	47	120	259
19.90	46	111	241
40.03	43	103	221
60.03	35	84	175
81.15	21	48	100
89.97	—	26	48

The vapor pressure isotherms (Fig. 6) take the form of curves concave toward the composition axis.

DISCUSSION OF RESULTS

The presence of clearly defined maxima on the viscosity, specific conductivity and corrected conductivity isotherms indicates that chemical reaction is taking place in the system. Evidence for this is also provided by the contraction observed in the system.

If we turn our attention to the viscosity isotherms (Figs. 1 and 2), then, as has already been pointed out, the viscosity maximum is shifted from 90 to 84 mole % C_6H_5OH as the temperature is lowered from 80 to 20°. If we consider that the shift of the maximum with fall in temperature proceeds slowly, it is easy to imagine that as the temperature is lowered further, the maximum will have a tendency to approach the ordinate 80 mole % C_6H_5OH. We are therefore inclined to think that the compound of composition $SnCl_4 \cdot 4\,C_6H_5OH$ is being formed in the system. We explain the formation of a compound of this composition in the same way as the formation of the compound $SnCl_4 \cdot 3\,CH_3COOH$ has been explained earlier [3]. The formation of the compound $SnCl_4 \cdot 4\,C_6H_5OH$ may be represented by the following equation:

$$[SnCl_4(C_6H_5O)_2]H_2 + 2C_6H_5OH \rightleftarrows [SnCl_4(C_6H_5O)_2]^{--} + 2C_6H_5OH_2^{+}.$$

The data on the vapor pressure of the system agree with this hypothesis of the composition and structure of the compound. Three ions are formed from four molecules of phenol, so that chemical reaction leads to a decrease in the depression. The association of the phenol acts in the same direction. Both factors lead to a positive deviation from Raoult's law.

The fact that the corrected conductivity maximum does not lie at 80 mole % C_6H_5OH, which would correspond to the composition suggested for the compound, but is displaced in the direction of greater phenol content, may be connected with the "relay" mechanism of the electrical conductivity, as a result of which the cation $C_6H_5OH_2^+$ in phenol shows a much greater mobility than the other ions. This should lead to an increase in the value of the corrected conductivity of mixtures containing excess phenol and consequently to a shift of the maximum, from the ordinate corresponding to the composition of the compound formed, to the phenol. Moreover, in mixtures rich in stannic chloride, the cation $C_6H_5OH_2^+$ cannot move by this mechanism since here there are no molecules which can bring about the transfer of the proton. It is difficult to imagine that the complex anion $[SnCl_4(C_6H_5O)_2]^{--}$ could move by this mechanism in an excess of $SnCl_4$ molecules.

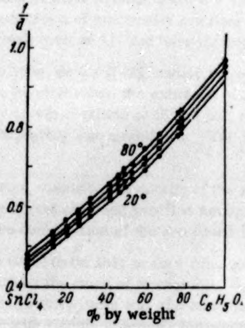

Fig. 5. Relationship between specific volume and composition.

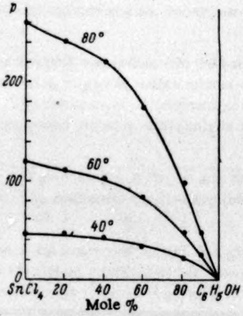

Fig. 6. Relationship between vapor pressure and composition.

The compound of stannic chloride and phenol is thermally unstable, as indicated in the diagram for the corrected conductivity (Fig. 4), which falls with increasing temperature as a result of the dissociation of the compound into components which do not conduct current. From a comparison of the corrected conductivity isotherms it may be assumed that at yet higher temperatures the system would become nonconducting, i.e., the compound formed would undergo complete thermal dissociation. This hypothesis is indirectly confirmed by the distillation of mixtures of stannic chloride and phenol. When the mixtures are heated, stannic chloride distills over first. When all the stannic chloride has distilled, boiling ceases, and the liquid only starts to boil again from 176° (phenol distills over). The compound formed is evidently completely dissociated at the boiling point of stannic chloride.

SUMMARY

1. A study has been made of the viscosity, density and electrical conductivity of the system $SnCl_4-C_6H_5OH$ at 20, 40, 60 and 80°.

2. The vapor pressure of the same system at 40, 60 and 80° has been studied.

3. Arguments have been put forward for the formation in this system of a compound of composition $SnCl_4 \cdot 4C_6H_5OH$. We ascribe to this compound the structure $[SnCl_4(C_6H_5O)_2]^{--} \cdot 2C_6H_5OH_2^+$.

4. A suggestion has been made concerning anomalous high mobility of the $C_6H_5OH_2^+$ cations in phenol.

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SYSTEMS FORMED BY STANNIC CHLORIDE WITH NITROBENZENE AND m-DINITROBENZENE

M. Usanovich and E. Pichugina

In 1927 Reihlen and Hake [1], described the interaction of stannic chloride and nitrobenzene. According to the data of these authors, there is a violent reaction between stannic chloride and nitrobenzene, resulting in the precipitation of practically colorless crystals, which fume in the atmosphere and are decomposed by water. The crystals melt at 11° and have the composition $SnCl_4 \cdot C_6H_5NO_2$.

In 1930, de Carli [2], studied the system $SnCl_4-C_6H_5NO_2$ for viscosity and fusion. On the basis of thermal analysis, he established the existence of a compound of composition $SnCl_4 \cdot C_6H_5NO_2$ which melted at −1°. The viscosity curves obtained at 15 and 25°, pass through a maximum. The existence of a compound of composition $SnCl_4 \cdot 2C_6H_5NO_2$ was established. The author mentions that the compound probably exists only in the liquid phase.

Later, viscosity and density of the system were studied by F. A. Yakovlev [3], at 30, 50 and 70°. The viscosity curves obtained pass first through an indefinite maximum. The author did not give any information at all on the composition of the compound formed.

In order to be able to draw conclusions about the composition of the compound formed in a given system, we undertook the study of this system. Apart from this, we studied the system stannic chloride − m-dinitrobenzene. The study of this system was of interest from the following considerations. It is known [4], that benzene does not combine with stannic chloride. Introduction of the nitro group into the benzene molecule results in interaction of nitrobenzene with stannic chloride. Therefore, we have reason to think that addition of nitrobenzene in $SnCl_4$ proceeds through the nitro group. It was desirable to find out the position of things with reference to the ratio of stannic chloride and nitrobenzene, in the molecule of which there exist two groups simultaneously, as a result of which addition may be produced.

EXPERIMENTAL

The system $SnCl_4-C_6H_5NO_2$ was studied for viscosity and density at 20, 40, 60 and 80°. On mixing the components, no heat effect was observed. Freshly prepared mixtures have a yellowish tint, which quickly changes to brown. Mixtures of stannic chloride with nitrobenzene did not crystallize on cooling to 0°.

The results of the viscosity measurements are given in Table 1.

The viscosity isotherms (Fig. 1) show a specific curve, passing through a maximum. With increasing temperature the maximum is displaced to the nitrobenzene side. In Table 1, the values for the viscosity temperature coefficient (B) are given, calculated according to the exponential formula. Curve B showing the dependence on composition (Fig. 2) passes through a maximum in the region of 67 mole % $C_6H_5NO_2$, indicating formation in the liquid phase of a compound of composition $SnCl_4 \cdot 2C_6H_5NO_2$. Measurements of the specific volume in dependence on composition (Fig. 3), result in a curve which is convex to the composition axis, i.e., there is condensation in the system. The density values are given in Table 2.

TABLE 1

$C_6H_5NO_2$ content (mole %)	Viscosity (in centipoises)				Viscosity temperature coefficient (B) (cal)
	20°	40°	60°	80°	
0.00	0.927	0.758	0.637	0.540	1836
29.97	1.37	0.975	0.764	0.630	3125
43.58	1.59	1.13	0.852	0.689	3142
46.78	1.68	1.16	0.878	0.695	3370
58.60	1.92	1.29	0.966	0.754	3592
72.42	2.11	1.41	1.04	0.806	3670
75.61	2.11	1.42	1.05	0.811	3588
88.64	2.10	1.45	1.09	0.840	3376
100.00	2.00	1.41	1.08	0.842	3162

TABLE 2

$C_6H_5NO_2$ (content (weight %)	Density			
	20°	40°	60°	80°
0.00	2.2340	2.1819	2.1288	2.0790
17.20	1.9882	1.9408	1.8955	1.8596
26.73	1.8535	1.8178	1.7763	1.7389
29.34	1.8257	1.7857	1.7485	1.7108
40.62	1.6953	1.6604	1.6213	1.5899
56.93	1.5315	1.5016	1.4707	1.4435
59.42	1.5101	1.4801	1.4539	1.4272
78.66	1.3517	1.3273	1.3050	1.2796
100.00	1.2080	1.1864	1.1680	1.1485

TABLE 3

Content $C_6H_4(NO_2)_2$		80°		100°		Viscosity temperature coefficient (B) (cal)
mole %	wt. %	$\eta \cdot 10^2$	d	$\eta \cdot 10^2$	d	
0.00	0.00	0.540	2.0790	0.471	2.0320	1788
25.01	17.71	0.807	1.9419	0.706	1.8940	2199
48.49	37.79	1.47	1.7678	1.09	1.7441	3343
62.83	52.18	1.89	1.6673	1.44	1.6260	3592
77.29	68.72	2.40	1.5647	1.82	1.5303	3868
93.94	90.98	2.98	1.4350	2.17	1.4080	4027
100.00	100.00	3.17	1.3928	2.31	1.3729	4108

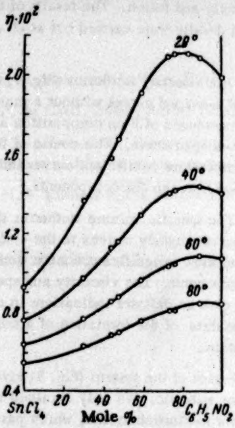

Fig. 1. Dependence of viscosity on composition.

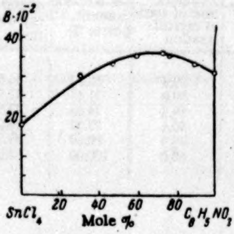

Fig. 2. Dependence of viscosity temperature coefficient on composition.

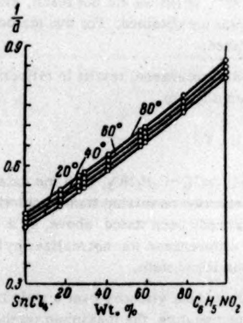

Fig. 3. Dependence of specific volume on composition.

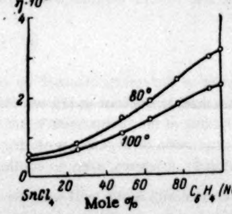

Fig. 4. Dependence of viscosity on composition.

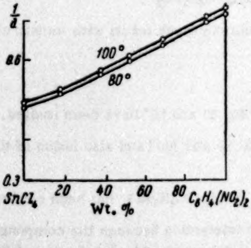

Fig. 5. Dependence of specific volume on composition.

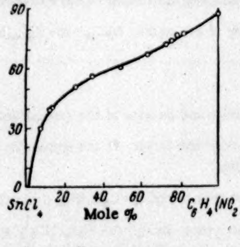

Fig. 6. Fusion diagram.

The system $SnCl_4 - m\text{-}C_6H_4(NO_2)_2$ was studied for viscosity, density and fusion. The results of the measurements are given in Tables 3 and 4. Measurements of viscosity and density were carried out at 80 and 100°. Below 80°, mixtures rich in m-dinitrobenzene, do not crystallize.

TABLE 4

$C_6H_4(NO_2)_2$ content (mole %)	Temperature of start of crystallization	$C_6H_4(NO_2)_2$ content (mole %)	Temperature of start of crystallization
7.42	29.5°	62.10	66.5°
11.85	39.0	71.45	71.5
12.47	39.5	74.35	73.5
25.01	50.5	77.29	76.0
33.61	55.5	80.50	76.5
48.49	60.0	100.00	87.5

The viscosity isotherms (Fig. 4) have the form of S-shaped curves without a maximum. The dependence of B on composition also results in an S-shaped curve. The course of the viscosity and temperature coefficient curves indicate interaction between the components.

The specific volume isotherms (Fig. 5) form curves slightly convex to the composition axis and show insignificant contraction on mixing the components. The viscosity and specific volume curves give no definite indications in the composition data of the formation of a compound in the system.

Fusion of the system (Fig. 6) gives a diagram with one eutectic. We only obtained a liquidus curve for m-dinitrobenzene, which passes practically through its own diagram. In the region of about 50 mole % $C_6H_5(NO_2)_2$, decomposition is observed in the liquidus curve, indicating a tendency to layer formation.

Since stannic chloride has a low crystallization temperature (−33°), which we did not reach, interruption of the eutectic, which must be observed at a still lower temperature, was not obtained. For this reason, comparison of the eutectic, which lies very close to $SnCl_4$, was not established.

Thus, existence of interaction between stannic chloride and m-dinitrobenzene, results in reflection on the viscosity and specific volume diagram, but is not reflected on the fusion diagram.

DISCUSSION OF RESULTS

A comparison of the results obtained by us for the system studied, $SnCl_4 - C_6H_5NO_2$, with the data of other authors, indicates that, in contrast to [1], we did not obtain a violent reaction on mixing stannic chloride with nitrobenzene. Mixing of the components is not accompanied, as has already been stated above, by a considerable heat effect. Precipitation of crystals on mixing stannic chloride with nitrobenzene was not realized by us, either. As mentioned already, mixtures, even on cooling to 0°, remained in the liquid state.

Our data on viscosity agree well with the data [2, 3]. Since we studied the viscosity over a wide range of temperature, there was the possibility of seeing that, with increasing temperature, the maximum on the viscosity isotherm is displaced to the side of the more viscous component − nitrobenzene. On the basis of the course of the viscosity temperature coefficient, we consider that in the given system, there is formation of a compound of composition $SnCl_4 \cdot 2C_6H_5NO_2$. We arrived at this result on the basis of de Carli's viscosity measurements [2]. We did not obtain any indication of the existence of a compound $SnCl_4 \cdot C_6H_5NO_2$.

The study of the system $SnCl_4 - m\text{-}C_6H_4(NO_2)_2$ showed that dinitrobenzene reacts with stannic chloride.

SUMMARY

1. Viscosity and density of the system $SnCl_4 - C_6H_5NO_2$ at 20, 40, 60 and 80° have been studied.

2. Viscosity and density in the system $SnCl_4 - m\text{-}C_6H_4(NO_2)_2$ at 80 and 100° and also fusion of this system, have been studied.

3. In the system $SnCl_4 - C_6H_5NO_2$, formation of the compound $SnCl_4 \cdot 2C_6H_5NO_2$ has been confirmed.

4. In the system $SnCl_4 - m\text{-}C_6H_4(NO_2)_2$, existence of chemical interaction between the components, has been established. No indications were obtained on the composition of the compound. Interaction of the component is not reflected on the fusion diagram.

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SOLUBILITIES IN THE SYSTEM POTASSIUM CHLORIDE – GLUCOSE – WATER AT 25°

A. K. Zhdanov and K. G. Higai

A number of authors [1-3] have established that organic substances have an effect on solubility and form of crystals of inorganic substances, which is sometimes of value for carrying out analytical determinations according to the precipitation method. For example, on precipitating calcium in the form of oxalate, addition of urea permits us to obtain large crystals of calcium oxalate. For elucidating the question of the dependence of solubility of inorganic substances on the presence of organic substances and also the effect of inorganic substances on the solubility of organic, it was of interest to study the solubility of some salts in presence of organic substances, over a wide range of concentration. In the present communication, results are given of a study of the solubility of potassium chloride in presence of glucose.

The solubility of glucose in water was studied by Jackson and Sibsbee [4]. They carried out determinations of the solubility of glucose in water at temperatures from −0.77 to 90.8° and found that the solubility of glucose increases with increase in temperature. Dehn [5] found that at 20°, the solubility of glucose is equal to 45.05 wt. %, or 82 g in 100 g water.

EXPERIMENTAL

In the present investigation the reaction was carried out at a fairly high state of purity. Water was twice distilled. As we had not met data on the solubility of glucose at 25°, special tests were carried out on the determination of solubility and density of a saturated solution of glucose in water at 25°. The solubility of glucose in water at 25° was shown to be equal to 49.95 wt. %, and the density of the saturated solution, 1.2210 g/ml.[*]

Preparation of the saturated solutions. Small amounts of glucose were introduced at constant temperature (25°) into a special container containing a saturated solution of potassium chloride. After mixing and attaining equilibrium, samples of saturated solution and precipitate were removed and an analysis carried out for glucose and potassium chloride contents in the solution and in the solid phase in equilibrium with it. After we took a sample of solution and bottom phase, a fresh portion of glucose was introduced into the vessel and after this manipulation, further samples of solution in the bottom phase, were removed. Similarly, into another vessel containing a saturated solution of glucose, small portions of potassium chloride were introduced and, after exactly the same manipulation, samples of solution and bottom phase were withdrawn.

It was established by special tests that in the first case, equilibrium was reached within 4-5 hours of the initial mixing. In the second case, equilibrium was established more slowly – after 6-8 hours. To make the method more reliable in the case of all the samples, the solutions were mixed for a period of 8-10 hours, after which the solution was left to stand for a further 1-2 hours.

Analysis of solutions and wet precipitates. The samples of solution and wet precipitates were analyzed for their glucose and potassium chloride contents. The water content was determined by difference. The potassium

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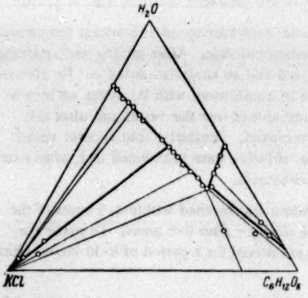
[*] According to reference-book data, the density of a saturated solution of glucose at 25° is equal to 1.544 g/ml. This value appears to be wrong.

Equilibrium in the system $KCl-C_6H_{12}O_6-H_2O$ at 25°.

Density of solutions	Composition of solutions (wt %)			Composition of residue (wt %)			Solid phase
	KCl	$C_6H_{12}O_6$	H_2O	KCl	$C_6H_{12}O_6$	H_2O	
1.1768	26.16	—	73.84	—	—	—	KCl
1.1800	25.90	0.86	73.24	—	—	—	
1.1962	25.28	5.44	69.28	—	—	—	
1.2014	24.59	7.68	67.73	95.08	0.81	4.11	
1.2120	23.79	10.61	65.60	94.26	0.88	4.86	
1.2251	23.24	14.16	62.60	—	—	—	
1.2310	22.60	15.26	62.14	—	—	—	
1.2392	21.90	17.59	60.51	—	—	—	
1.2720	20.50	26.92	52.58	—	—	—	
1.2790	20.02	28.79	51.19	—	—	—	
1.2860	19.55	31.19	49.26	81.83	6.80	11.37	
1.2990	18.98	34.04	46.98	—	—	—	
1.3070	18.31	36.77	44.92	—	—	—	
1.3200	17.73	39.72	42.55	—	—	—	
1.3350	16.96	43.46	39.58	88.08	5.57	6.35	
1.3510	16.17	47.94	35.89	—	—	—	
1.3800	15.24	51.31	33.45	17.20	67.75	15.05	$KCl + C_6H_{12}O_6$
1.3800	14.89	52.67	32.44	6.40	79.56	14.04	
1.3790	13.00	52.64	34.36	2.45	83.32	14.23	$C_6H_{12}O_6 \cdot H_2O$
1.3130	9.55	50.94	39.51	3.71	78.38	17.91	
1.2895	6.69	51.40	41.91	—	—	—	
1.2445	3.32	50.06	46.62	—	—	—	
1.2210	—	49.95	50.05	—	—	—	

chloride content was determined by a potentiometric method by titrating the samples with 0.1 N silver nitrate solution, with a silver indicator electrode. The glucose content was determined by the Bugo [6] soda method, based on oxidation of glucose to gluconic acid by hypoiodite. In this case, a weighed sample was transferred to a 250 ml graduated flask and an aliquot part taken for analysis. To the solution under analysis were added 25 ml 0.1 N iodine solution and 15 ml 1 N soda solution. After we let the mixture stand for 20-30 minutes, the solution was acidified with sulfuric acid and the excess iodine titrated with 0.1 N thiosulfate solution.



Isothermal section of diagram of state of the system $KCl-C_6H_{12}O_6-H_2O$.

The results obtained by us for the determination of the solubility in the system potassium chloride-glucose-water are given in the table and are represented in the figure.

As seen from the table, the density of the solution increases according to the amount of glucose added to the saturated potassium chloride solution, and reaches a very high value at the eutectic point. Addition of glucose to a saturated solution of potassium chloride slightly lowers the solubility of potassium chloride. On addition of potassium chloride to a saturated solution of glucose, the density of the solutions also increases up to the eutectic point. The solubility of glucose in presence of potassium chloride increases slightly up to the eutectic point, where a very high value is reached. In this respect the behavior of glucose is similar to sugar, the solubility of which increases on addition of certain salts.

The solid phases which are in equilibrium with the saturated solutions in the ternary system potassium chloride–glucose–water, are represented by potassium chloride for solutions saturated with potassium chloride; and, correspondingly, the monohydrate of glucose for saturated solutions of glucose. At the eutectic point the solution is saturated with potassium chloride and glucose and contains 15.06% potassium chloride and 51.99% glucose, and is in equilibrium with the solid phase consisting of a mixture of potassium chloride and glucose.

SUMMARY

1. Solubility in the system potassium chloride–glucose–water has been determined at 25°.

2. Solubility and density determinations of a saturated solution of glucose in water at 25° have been carried out.

3. It has been established that in the system potassium chloride–glucose–water, neither molecular compounds nor solid solutions are formed, and a eutectic solution containing 15.06% potassium chloride and 51.99% glucose is formed.

4. The density of the solution increases with addition of glucose to a saturated solution of potassium chloride, as well as on adding potassium chloride to a solution of glucose, and reaches a very high value at the eutectic point.

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giving an admixture of potassium [illegible] worsened. In this respect the [illegible] are not valid.

The solid phases [illegible] water, [illegible] the [illegible] solution [illegible] and is in equilibrium with the [illegible]

SUMMARY

1. Solubility in the system potassium chlorate [illegible]

2. Solubility and density determinations of a saturated solution [illegible] have been carried out.

3. It has been established that in the system potassium chlorate [illegible] chlorate is formed.

4. The density of the saturated [illegible] potassium chlorate, as well as [illegible] eutectic point.

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[5] [illegible]

[6] [illegible]

Received [illegible] Central Asia State University

COMPARATIVE STUDY OF METAL COMPLEXES WITH TARTARIC, SUCCINIC AND DIMETHOXYSUCCINIC ACIDS

I. V. Pyatnitsky and S. M. Gendler

Complex formation of cations of heavy metals with hydroxy acids of the aliphatic series in alkaline solutions is usually explained by replacement of hydrogen of the alcoholic group by the metal. This explanation agrees with the usual theoretical views and is confirmed by experimental data. It is known that aromatic hydroxy acids and alcohols are capable of reacting with metal cations and eliminating hydrogen from the hydroxyl group: these reactions are characteristic, for example, of salicylic acid [1], phenols and other substances. Interaction is explained by the fact that the phenyl radical reinforces the acidic properties of the hydroxyl hydrogen. In the case of aliphatic acids, the capacity for this hydrogen replacement is shown to a low degree; nevertheless, it exists. In a number of works of a preparative nature [2-4], complexes of metals with hydroxy acids were submitted to elementary analysis and in some cases [5] were obtained in the anhydrous state, and on the basis of such an analysis, it was possible to obtain results on the replacement of alcoholic hydrogen by metals. It has also been established that acids of the aliphatic series, not containing alcoholic hydroxyl, lose their power of complex formation in alkaline solution [6], which also indicates strongly the existence of the role of the hydroxyl group in the process. Finally, it was found [7], that malic acids in which the hydroxy group has been replaced by bromine or an amino group, or hydrogen of the hydroxyl by the CH_3 radical, are not in a position to retain aluminum hydroxide in ammoniacal solution.

Thus, up to now there has been evidence of complex formation of metals with hydroxy acids of the aliphatic series which has been considered as sufficiently probable. In spite of this, recently another way has been put forward [8-10], in accordance with which compounds of the type $[C_4H_4O_6Me(OH)_2]K_2$ are formed in alkaline solution.

Proof of this is seen by the authors in the fact that, for example, on dissolving copper tartrate in alkali, for each molecule of the former, two molecules of alkali are used up; therefore the process of solution goes according to the following:

$$CuC_4H_4O_6 + 2OH^- = [C_4H_4O_6Cu(OH_2)]^{--}.$$

However, the reaction may be expressed by an equation based on substitution of hydroxyl hydrogen by copper cation:

$$CuC_4H_4O_6 + 2OH^- = CuC_4H_2O_6^{--} + 2H_2O.$$

It is easy to see that the choice between these two reactions cannot be made solely on the basis of the number of molecules of alkali concerned in dissolving the precipitate; we were therefore interested in carrying out an investigation of the nature of complex formation by methods other than these, in order to elucidate the role of oxygen and hydrogen of the hydroxy group, in the process. There has been practically no work of a suitable nature on hydroxy acids of the aliphatic series if we do not take into account the references to earlier preparative investigations.

The object of our work was to carry out a comparative study of complex formation of metals with tartaric, succinic and dimethoxysuccinic acids in solution. These acids were chosen as a result of the fact that they all have a chain of four carbon atoms and contain two carboxyl groups; however, at the same time, tartaric acid has two hydroxyl groups, in dimethoxysuccinic acid the hydrogen atoms of both hydroxyl groups are replaced by methyl radicals, and in succinic acid there are no hydroxyl groups.

EXPERIMENTAL

Synthesis of dimethoxysuccinic acid [11]. In a flask with a reflux condenser were placed 50 g dry silver oxide and 205 g methyl iodide ; the mixture was boiled for 2 hours, while adding small amounts of dry silver tartrate (total, 24 g). Excess methyl iodide was distilled off on a water bath, the residue extracted with ether in a Soxhlet apparatus for a period of 3 hours. After evaporation of the ether, the dimethyl ester of dimethoxysuccinic acid $COOCH_3CHOCH_3CHOCH_3COOCH_3$ was obtained in the form of a liquid which was extremely difficult to crystallize. For crystallization, in one case cooling with liquid air was carried out; in another experiment, distillation at 132°C (12 mm) was carried out. The melting point of the preparation was 51°, which corresponds to data in the literature [12].

A weighed amount of the dimethyl ester was dissolved in water and saponified:

$$(COOCH_3)_2(CHOCH_3)_2 + 2NaOH = COONaCHOCH_3CHOCH_3COONa + 2CH_3OH.$$

For further experiments the solution obtained was used immediately; concentration of sodium dimethoxysuccinate in it was equal to 0.1 M.

Qualitative tests in alkaline solutions. Interaction of tartaric, succinic and dimethoxysuccinic acids was studied with cations of heavy metals in alkaline solution, 0.1 M solutions of the nitrates of Al, Fe, Co, Cd, Cu, Pb, and sulfates of Ni and Ti being used. To 1 ml 0.1 M solution of the salt of the corresponding metal was added 6 ml 0.1 M solution of the acid under test and then a solution of caustic soda or ammonium hydroxide of the same titer, in order to have a subsequent concentration in the final solution of 0.1 M in one series of tests, and 0.01 M in the other. A solution of caustic soda was used for cations of iron, bismuth, nickel, cadmium, copper and titanium, and a solution of ammonium hydroxide for cations of aluminum, iron, bismuth, lead and titanium. The usual final volume of solution was 20 ml.

These qualitative tests gave the following results. In presence of tartaric acid, a precipitate of the corresponding metal hydroxide was not formed in a single case; all the solutions were quite clear and remained so for an indefinite time. In presence of succinic acid, a precipitate of the hydroxide came down immediately. Dimethoxysuccinic acid was somewhat original; in some cases the precipitate came down immediately, however, sometimes precipitation was slow and just after adding the solution of alkali or ammonium hydroxide, the solution remained clear. However, after a short time the solution became turbid and a precipitate of the hydroxide gradually separated. Adding a solution of a strong electrolyte – sodium nitrate – hastened the precipitation. A completely satisfactory coagulating effect was not observed in presence of tartaric acid.

Qualitative Study of Complexes of Iron (III) with Tartaric, Succinic and Dimethoxysuccinic Acid.

1. Tartrate complex of iron. Paira [5] isolated an anhydrous tartrate complex of iron in the solid form and on the basis of its analysis, gave it the formula $H[FeC_4H_2O_6]$. We studied [13] the properties of the tartrate complex of iron in solution at a pH of 4-6, and showed that its composition and structure correspond to the formula written above. France [14] studied this complex in a more acid medium; he showed that on mixing hot 5 M solutions of ferric chloride and tartaric acid, a lemon-yellow crystalline precipitate separates, analysis of which indicates that very probably, it has the following formula: $Fe(H_2O)_3HC_4H_4O_6Cl_2$.

Data are given below relating to a study of the composition and stability of the tartrate complex of iron formed in solution at pH 1-3.

a) Determination of composition. Composition was determined according to the Ostromislensky–Zhob isomolar series. The optical density of the yellow-tinted solutions was determined in an FM photometer with color filter No. 7 (effective wave length 465 mμ). Volume of solution 50 ml, 5 cm thick cell. The results of the experiments are given in Fig. 1.

It is seen from Fig. 1 that the maximum optical density corresponds to a molar ratio of iron to tartaric acid of 1: 1, i.e., the complex contains 1 molecule of tartaric acid to 1 atom of iron. This result is also confirmed by measurements of color absorption of solutions containing constant amounts of ferric nitrate solution and increasing amounts of tartaric acid solution. Acidity of solution, 0.01 M, usual volume 50 ml; in all the experiments 7 ml 0.01 M ferric nitrate solution was taken. Figure 2 shows that the bend in the curve corresponds to a molar ratio of iron and tartaric acid of 1: 1.

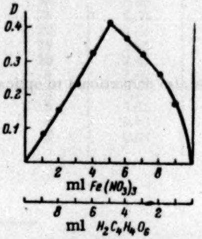


Fig. 1. Determination of composition of iron tartrate complex at pH 2.

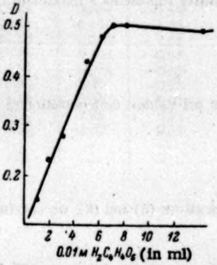


Fig. 2. Dependence of optical density of ferric nitrate solution on tartaric acid concentration.

b) Determination of structure. The number of hydrogen ions taking part in complex formation was determined [1]. For this, the dependence of optical density of the solution of the complex on pH of the medium, was determined. The reaction of formation of the complex may be represented by the following equation:

$$Fe^{+3} + H_4T \rightleftarrows FeH_{4-n}T^{+3-n} + nH^+. \tag{1}$$

Here n is the number of hydrogen ions which separate on reaction of each iron ion with a molecule of tartaric acid; T is the residue of molecules of tartaric acid.

The equilibrium constant of this reaction is equal to:

$$K_{eq} = \frac{[FeH_{4-n}T^{+3-n}][H^+]^n}{[Fe^{+3}][H_4T]}. \tag{2}$$

Applying logarithms, we obtain:

$$\log \frac{[FeH_{4-n}T^{+3-n}]}{[Fe^{+3}]} = \log K_{eq} - n\log[H^+] + \log[H_4T]. \tag{3}$$

Differentiating according to log $[H^+]$, we find: *

$$-\frac{d\log\frac{[FeH_{4-n}T^{+3-n}]}{[Fe^{+3}]}}{d\log[H^+]}=n. \tag{4}$$

Thus, for calculating n we have to determine experimentally the dependence of log $\frac{[FeH_{4-n}T^{+3-n}]}{[Fe^{+3}]}$ on pH. Corresponding concentrations of combined and uncombined iron in the complex, for varying pH, may be found by determining the optical density of solutions of iron tartrate. We can assume that the pH value at which the optical density represents a maximum corresponds to the total combined iron in the complex. Then

$$C_{Fe\ comb.}=kD_{max}. \tag{5}$$

At lower pH values, concentration of combined iron in the complex is also proportional to optical density:

$$[FeH_{4-n}T^{+3-n}]=kD. \tag{6}$$

From Equations (5) and (6), we obtain:

$$[FeH_{4-n}T^{+3-n}]=\frac{D}{D_{max}}C_{Fe\ comb}. \tag{7}$$

The concentration of uncombined iron in the complex may be found from the equation:

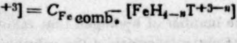
$$[Fe^{+3}]=C_{Fe\ comb.}-[FeH_{4-n}T^{+3-n}]. \tag{8}$$

To 1.5 ml 0.1 M ferric nitrate solution was added 5 ml 0.25 M tartaric acid solution and varying amounts of a solution of nitric acid, then water was added up to 50 ml, and the optical density of the solutions measured. The results obtained are given in Table 1.

The data in Table 1 are represented graphically in Fig. 3. On the ordinate are plotted the amounts log $\frac{[FeH_{4-n}T^{+3-n}]}{[Fe^{+3}]}$, and on the abscissa the pH. The tangent of the oblique angle to the straight line is 2.3. It follows from this that the reaction between tartaric acid and trivalent iron ions in an acid medium, proceeds with separation of two hydrogen ions and, apparently, partly by replacement of the third hydrogen atom.

It was shown earlier [13] that iron on electrolysis of a tartaric acid solution (pH 3) migrates mainly to the cathode.

Comparing this fact with the data given in Table 1 and also with the results of determination of composition, we can come to the conclusion that tartaric acid forms with trivalent iron ions, in acid solution, mainly complex cations of the following structure:



$$\underbrace{(OOCCH(OH)CH(OH)COO)^+}_{Fe}$$

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* If there is excess tartaric acid compared with the iron concentration, we can take $[H_4T]$ = constant.

TABLE 1

Optical Density of Solutions of Iron Tartrate Complex for Different Acidities.

ml N HNO_3 solution added	$[H^+]\cdot 10$	pH	D	$[FeH_{4-n}T^{+3-n}]\cdot 10^4$	$[Fe^{+3}]\cdot 10^4$	$\frac{[FeH_{4-n}T^{+3-n}]}{[Fe^{+3}]}$	$\log\frac{[FeH_{4-n}T^{+3-n}]}{[Fe^{+3}]}$
40	8.03	0.09	0.02	0.77	29.23	0.026	—1.58
30	6.03	0.22	0.035	1.34	28.66	0.047	—1.33
25	5.03	0.30	0.07	2.68	27.32	0.098	—1.01
20	4.03	0.39	0.10	3.85	26.15	0.146	—0.84
15	3.03	0.51	0.15	5.75	24.25	0.238	—0.62
10	2.03	0.69	0.29	11.10	18.90	0.59	—0.23
8	1.63	0.78	0.39	14.90	15.10	0.98	—0.01
6	1.23	0.90	0.51	19.50	10.50	1.85	0.27
5	1.03	0.98	0.63	24.10	5.90	4.07	0.61
4	0.83	1.07	0.78	30.00	—	—	—
3	0.63	1.18	0.78	—	—	—	—

Note. Color filter No. 7, 5 cm thick cell.

c) Determination of instability constant. The instability constant (K_i) of the complex may be calculated from the data in Table 1. It was found that higher up, $n \approx 2$; therefore the equilibrium constant of Reaction (1) is equal to:

$$K_{eq}=\frac{[FeC_4H_4O_6^+][H^+]^2}{[Fe^{+3}][H_2C_4H_4O_6]}=\frac{K_1K_2}{K_i}, \tag{9}$$

where K_1 and K_2 are the first and second dissociation constants of tartaric acid. From Equation (9) and expressions of the acid dissociation constant of tartaric acid, it follows that:

$$K_i=\frac{[Fe^{+3}][C_4H_4O_6^{-2}]}{[FeC_4H_4O_6^+]}=\frac{K_1K_2}{K_{eq}}. \tag{10}$$

The calculated figures for the equilibrium constants may be found with very great accuracy from those experiments in Table 1 in which the ratio of combined and uncombined iron in the complex is close to unity. From column 7 in Table 2, we find:

$$K_{eq}=\frac{14.9\cdot 10^{-4}\,(1.63\cdot 10^{-1})^2}{15.1\cdot 10^{-4}\cdot 2.5\cdot 10^{-2}}=1.04,$$

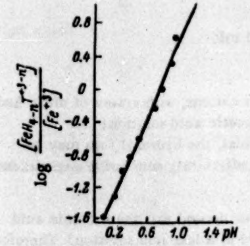
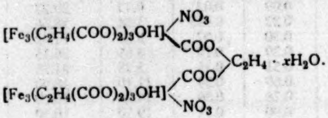


Fig. 3. Dependence of logarithm of ratio of concentration of tartaric acid complex and free iron ions on pH.

from which we obtain for the instability constants:

$$K_1 = \frac{1.04 \cdot 10^{-3} \cdot 4.55 \cdot 10^{-5}}{1.04} = 4.55 \cdot 10^{-8}.$$

2. Succinic acid complex of iron. Weinland and Paschen [15], isolated iron succinate by dissolving succinic acid and ferric nitrate in hot 96% alcohol and subsequently cooling the solution obtained. On the basis of the analysis of the isolated brown-colored powder, for iron, nitrogen and carbon, the authors attributed to this substance the following formula:



$$\begin{matrix}[Fe_3(C_2H_4(COO)_2)_3OH] \begin{matrix} NO_3 \\ COO \end{matrix} \\ [Fe_3(C_2H_4(COO)_2)_3OH] \begin{matrix} COO \\ NO_3 \end{matrix} \end{matrix} C_2H_4 \cdot xH_2O.$$

TABLE 2

Composition of Succinic Acid Complex of Iron at pH 3.

Milliliters of solution taken			Molar ratio Fe : $H_2C_4H_4O_4$	Optical density of mixtures of solutions of ferric nitrate and succinic acid	Optical density of ferric nitrate	Δ
0.1 M succinic acid	0.1 M $Fe(NO_3)_3$ and 0.01 N HNO_3	0.01 M HNO_3				
1	2	3	4	5	6	7
0.5	4.5	—	9 : 1	0.42	0.34	0.08
1.0	4.0	0.5	4 : 1	0.49	0.31	0.18
1.5	3.5	1.0	7 : 3	0.59	0.27	0.32
2.0	3.0	1.5	3 : 2	0.63	0.22	0.41
2.5	2.5	2.0	1 : 1	0.67	0.18	0.49
3.0	2.0	2.5	2 : 3	0.59	0.13	0.46
3.5	1.5	3.0	3 : 7	0.47	0.08	0.39
4.0	1.0	3.5	1 : 4	0.38	0.05	0.33
4.5	0.5	4.0	1 : 9	0.22	0.03	0.19

Note. Color filter No. 7, 5 cm thick cell, volume of solution, 50 ml.

They regarded this compound as a salt formed by complex multinuclear cations, with anions of nitric and succinic acids, similar to the multinuclear cations which chromium gives in acetic acid solution: $[Cr_3(CH_3COO)_6]^{+3}$, since, being situated in the internal zone of the acetic acid radical, the hydroxyl ions may be partially replaced. It should be mentioned that the authors have not found sufficiently conclusive experimental confirmations for such a structure.

a) Determination of composition and structure. Preliminary experiments showed that the succinic acid complex of iron is not colored so intensely as the tartaric acid and is formed in a less acid solution. Therefore, for determining the composition according to the method of isomolar series, we used a more concentrated solution of ferric nitrate and carried out the measurements at a low acidity.

The results of the measurements are given in Table 2.

In column 6 of Table 2, the optical density of a solution of ferric nitrate, without adding succinic acid solution, is given. It is seen from these data that the intensity of the specific color of the ferric nitrate solution (as a result of hydrolysis) is fairly marked; therefore, for constructing the curve, composition – optical density, represented in Fig. 4, we used the figures in the last (7) column of the table, which represent the difference between the figures in columns 5 and 6.

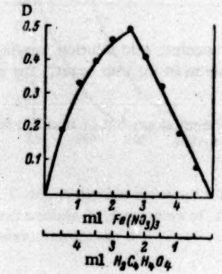


Fig. 4. Determination of succinic acid complex of iron at pH 3.

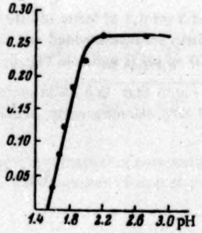
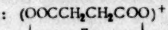


Fig. 5. Dependence of optical density of succinic acid solution of iron on pH.

It is seen from Fig. 4 that the maximum optical density corresponds to a molar ratio of the components equal to unity. Experiments on ion transfer showed that, on electrolysis, iron migrates to the cathode exclusively. For these experiments a mixture of 2 ml 0.1 M ferric nitrate solution with 6 ml 0.25 M succinic acid solution was used and water added up to 250 ml. Comparing these facts, we come to the conclusion that iron combines with succinic acid in solution in a complex of the following structure:



$$\underbrace{(OOCCH_2CH_2COO)}_{Fe}{}^{+}$$

.

b) Determination of instability constant. The equilibrium constant of the reaction of formation of the complex is expressed by the equation:

$$Fe^{+3} + H_2C_4H_4O_4 \rightleftarrows FeC_4H_4O_4^{+} + 2H^{+}, \tag{11}$$

from which

$$K_{eq} = \frac{[FeC_4H_4O_4^{+}][H^{+}]^2}{[Fe^{+3}][H_2C_4H_4O_4]} = \frac{K_1K_2}{K_i} \tag{12}$$

and the instability constant is equal to:

$$K_i = \frac{K_1K_2}{K_{eq}} = \frac{[Fe^{+3}][C_4H_4O_4^{-2}]}{[FeC_4H_4O_4^{+}]}. \tag{13}$$

We found the equilibrium constant by the method described for the tartaric acid complex by determining the pH value at which an optical density is reached, equal to half the maximal. At this acidity, half the usual amount of iron is combined in the complex and the other half is present in the form of free ions, i.e.,

$$\frac{[FeC_4H_4O_4^+]}{[Fe^{+3}]}=1. \tag{14}$$

Therefore

$$K_{eq}=\frac{[H^+]^2}{[H_2C_4H_4O_4]}. \tag{15}$$

To a mixture of 3 ml 0.1 M ferric nitrate solution and 10 ml 0.25 M succinic acid solution, varying amounts of a 1 N solution of nitric acid were added and the mixture was then made up to 50 ml with water. The dependence of the value of D on pH is shown in Fig. 5.

It is seen from Fig. 5 that in 0.05 M succinic acid solution, half of the usual amount of iron is combined in the complex at pH 1.78. Consequently, according to (15):

$$K_{eq}=\frac{(1.65\cdot 10^{-2})^2}{5\cdot 10^{-2}}=5.45\cdot 10^{-3},$$

and the instability constant, in agreement with Equation (13), is equal to:

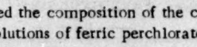
$$K_i=\frac{6.9\cdot 10^{-5}\cdot 2.5\cdot 10^{-6}}{5.45\cdot 10^{-3}}=3.2\cdot 10^{-8}.$$

3. Dimethoxysuccinic acid complex of iron. a) Determination of composition. Preliminary experiments showed that on adding a solution of sodium dimethoxysuccinate to a solution of ferric nitrate in an acid medium, a yellowish-colored solution is formed similar to the color in a solution of the tartaric acid complex of iron. We determined the composition of the compound obtained by the method of isomolar series, in a spectrophotometer SF-4. Solutions of ferric perchlorate were used and there was marked color absorption in the shorter-wavelength region of the nitric acid anion. For selecting the most suitable wave length, first, the color absorption curves for ferric perchlorate and the dimethoxysuccinic acid complex of iron were determined. These curves are represented in Fig. 6. Curve 1 relates to a mixture of 0.5 ml 0.1 M sodium dimethoxysuccinate solution with 0.5 ml 0.1 M ferric perchlorate solution, diluted to 5 ml; concentration of perchloric acid in this solution was equal to 0.033 N. Curve 2 gives measurements of the optical density of 0.01 M ferric perchlorate solution in 0.053 N perchloric acid. It is seen from the figure that the maximum color absorption of the dimethoxysuccinic acid iron complex is at a wavelength of 330 mμ; however, at this wavelength the measurements are not satisfactory, since the color absorption of ferric perchlorate solution under these conditions is fairly marked. We carried out further measurements at a wavelength of 380 mμ, where the absorption of ferric perchlorate solution may be regarded as negligible.

The results of the determinations are shown in Fig. 7.

It is seen from Fig. 7 that the maximum optical density is reached for a ratio Fe: $H_2C_6H_8O_6$ = 1:1, i.e., for a composition of the complex of 1 atom of iron to 1 molecule of dimethoxysuccinic acid.

Experiments were also carried out on ion transfer. To 0.25 ml 0.1 M ferric nitrate solution was added 2.5 ml 0.1 M sodium dimethoxysuccinate solution and water added to 25 ml. On electrolysis of this solution, the pH of which was equal to 2.35, it was shown that part of the iron is transferred to the cathode space. Taking into consideration the composition of the complex, it may be said that its structure is represented by the following formula:



$$\left[\underbrace{OOC\,(CHOCH_3)_2\,COO}_{Fe}\right]^+.$$

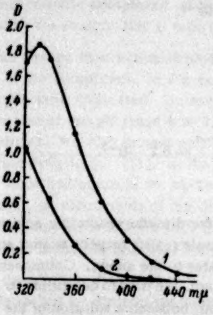


Fig. 6. Color absorption curves of solutions of dimethoxysuccinic acid complex of iron (1) and ferric perchlorate (2).

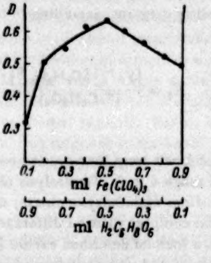


Fig. 7. Determination of composition of dimethoxysuccinic acid complex of iron at pH 1.6.

b) Determination of instability constant. The instability constant of the complex was determined by the method described above. From Equation (10), it is seen that, for calculating K_I, it is necessary to know the first and second dissociation constants of the acid; therefore we first determined K_1 and K_2 for dimethoxysuccinic acid. To 10 ml 0.1 M solution of sodium dimethoxysuccinate was added 10 ml 0.1 N hydrochloric acid solution and the pH of the acid salt obtained determined by the potentiometric method. It was shown to be equal to 3.55. Then to this solution was added another 5 ml hydrochloric acid and the pH of this buffered solution, containing dimethoxysuccinic acid and its acid salt, in equal concentrations was determined again. For the measurements, we obtained a pH of 2.90. From these data we calculated the value of the corresponding constants according to the equations:

$$\mathrm{pH} = \mathrm{p}K_1 + \log\frac{C_{\mathrm{salt}}}{C_{\mathrm{acid}}} \tag{16}$$

and

$$\mathrm{pH} = \frac{\mathrm{p}K_1 + \mathrm{p}K_2}{2} \tag{17}$$

from which $\mathrm{p}K_1 = 2.90$, $K_1 = 1.25 \cdot 10^{-3}$, $\mathrm{p}K_2 = 4.20$ and $K_2 = 6.3 \cdot 10^{-5}$.

On comparing these figures with the values of the dissociation constants of tartaric acid ($K_1 = 1.04 \cdot 10^{-3}$ and $K_2 = 4.55 \cdot 10^{-5}$), it is seen that substitution of the hydrogen atoms by methyl radicals has practically no effect on the dissociation of the acid.

The optical density of iron dimethoxysuccinate solutions was then measured at different pH values. To 0.5 ml 0.1 M ferric nitrate solution 5 ml 0.1 M sodium dimethoxysuccinate solution was added, and varying amounts of a 1 N solution of nitric acid, and then water added up to 30 ml. The results of the optical density measurements of these solutions, in the FM photometer, are given in Fig. 8.

It is seen from Fig. 8, that in $1.67 \cdot 10^{-2}$ M dimethoxysuccinic acid solution, half of the total ferric nitrate is combined in the complex at pH 1.4. Consequently, the equilibrium constant of the reaction of formation of the complex, in agreement with Equation (15), is equal to:

$$K_{eq}=\frac{[H^+]^2}{[H_2C_6H_8O_6]}=\frac{(4\cdot10^{-2})^2}{1.67\cdot10^{-2}}=9.6\cdot10^{-2}.$$

The instability constant, according to (13) is equal to:

$$K_1=\frac{[Fe^{+3}][C_6H_8O_6^{-2}]}{[FeC_6H_8O_6]^+}=\frac{K_1K_2}{K_{eq}}=\frac{1.25\cdot10^{-3}\cdot6.3\cdot10^{-5}}{9.6\cdot10^{-2}}=8.2\cdot10^{-7}.$$

Some experiments were then carried out with reference to a study of the dimethoxysuccinic acid complex of iron in the pH range 4 to 6. Electrolysis of a 0.001 M solution of the complex with respect to iron, and 0.01 M with respect to sodium dimethoxysuccinate, showed that at pH 5, iron migrates to the anode. Consequently, the composition of the complex must be different from that in a more acid medium. We tried to determine its composition according to a method described earlier [13], by studying the equilibrium between a solution of the disalicylate complex of iron and a solution of sodium dimethoxysuccinate. However, it was shown that, unlike the tartaric acid solution, sodium dimethoxysuccinate, even with a marked excess, does not decolorize a solution of iron disalicylate.

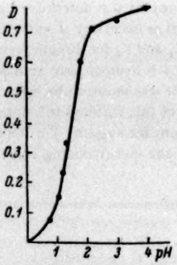


Fig. 8. Dependence of optical density of iron dimethoxysuccinate solution on pH.

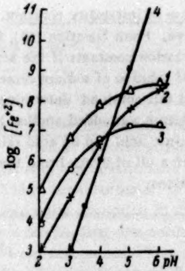


Fig. 9. Dependence of negative logarithm of concentration of iron ions on pH in solutions of tartaric (1), succinic (2) and dimethoxysuccinic (3) acid complexes of iron in a saturated solution of ferric hydroxide (4).

DISCUSSION OF RESULTS

From the experimental material given above, it is seen that, in acid solution (pH 1-3) all three acids behave similarly to each other; they give complexes with iron, of a similar composition and approximately the same stability. To illustrate this, in Fig. 9, curves 1, 2 and 3 give characteristic variations in the negative logarithm of the concentration of iron ions with pH for solutions of tartaric, succinic and dimethoxysuccinic acid complexes of iron, respectively. The curves were constructed for cases when the usual concentration of each acid is equal to 0.1 M, and the usual concentration of the complex is 0.01 M. The straight line 4, expresses the dependence of log $[Fe^{+3}]$ on pH (calculated from the value of the solubility product for a saturated solution of ferric hydroxide. It is seen from Fig. 9 that the course of the curves is practically identical for all three complexes. This is explained by the fact that only carboxylic groups of acids take part in complex formation; the effect of oxygen and hydrogen of the hydroxy group, here again, is inconclusive. It also follows from Fig. 9, that cationic complexes of composition FeA^+ can be stable only up to pH about 4.2-4.6; this is seen from the fact that the straight line 4 intersects all three curves, namely at this pH value.

If no change in structure is produced at an increased pH, then ferric hydroxide must be precipitated from solutions of the complexes. In the case of the succinic acid complex, this is observed in action; it is stable only up to the pH value indicated. However, tartaric and dimethoxysuccinic acids inhibit precipitation of ferric hydroxide also at the pH range 4 to 7. In both cases this is linked with variation in composition or structure of the complexes. We also showed earlier that tartaric acid at this pH range forms a more stable complex of composition $FeC_4H_2O_6^-$ [13]. In the case of dimethoxysuccinic acid, conversion to such a structure is not strictly possible, since hydrogens of the hydroxy groups have been replaced by methyl radicals. Taking into consideration the fact that, on electrolysis of the dimethoxysuccinic acid complex, iron migrates to the anode, it can be assumed that here a complex is formed with the proportion $Fe : H_2C_6H_8O_6 = 1 : 2$. Introduction of methoxy groups into the succinic acid molecule increases the capacity for complex formation.

In the alkaline field (pH > 7), the capacity for retaining iron (and also cations of other metals) in solution, has also been lost by dimethoxysuccinic acid. Oxygen of the hydroxy group is capable apparently, of forming colloidal solutions as in the precipitation of hydroxides, only in the presence of sodium dimethoxysuccinate, and with some difficulty. Stable alkaline solutions are produced only in presence of tartrates. This difference in behavior of tartaric and dimethoxysuccinic acids in alkaline solutions is not capable of being explained other than by chemical nonintervention of hydrogens of hydroxy groups, in the reaction, from which it follows that the process of complex formation consists of substitution of these hydrogens by cations of heavy metals.

SUMMARY

1. Behavior of cations of iron, aluminum, bismuth, titanium, copper, lead, nickel, cobalt and cadmium in presence of an excess of tartaric, succinic and dimethoxysuccinic acids in alkaline and ammoniacal solutions has been studied. It is shown that stable solutions are produced only in presence of tartrates; succinic acid does not hinder precipitation of the hydroxides of the elements enumerated, and dimethoxysuccinic acid only inhibits slightly the capacity for forming colloidal solutions. Differences in behavior of tartaric and dimethoxysuccinic acids show that the process of complex formation in alkaline solution leads to substitution of hydrogen atoms of alcoholic groups of hydroxy acids by cations of heavy metals.

2. Composition, structure and stability of tartaric, succinic and dimethoxysuccinic acid complexes of iron in acid solution (pH 1-3) have been studied by the optical method. It has been shown that in all cases cationic complexes are formed of a similar composition, and approximately the same stability, at the expense of substitution of hydrogen atoms of carboxylic groups of the corresponding acids, by iron cations. Instability constants of these complexes have been determined.

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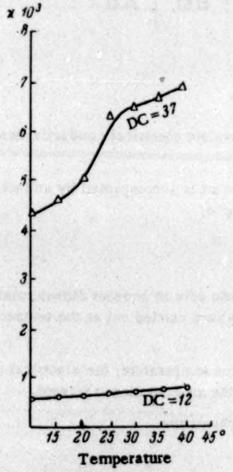
PHYSICOCHEMICAL STUDY OF AQUEOUS DIOXAN SOLUTIONS

IX. AQUEOUS DIOXAN SOLUTIONS OF SULFURIC ACID

R. F. Mezhennyi

The properties of solutions of hydrogen chloride in dioxan [1], and in aqueous dioxan mixtures [2] and also sulfuric acid solutions in dioxan [3], were described earlier. In the present work the electrical conductivity of sulfuric acid in aqueous dioxan mixtures is studied.

It has been shown [3], that sulfuric acid solutions in dioxan, not only at low, but even at considerable concentrations (~10 mole %) are very bad conductors of electricity. Even for sulfuric acid concentrations of 2.48 N, the equivalent electrical conductivity of sulfuric acid solutions in dioxan is equal to 0.0238 Ω^{-1}. For aqueous solutions of 2 N concentration, the equivalent electrical conductivity of sulfuric acid reaches about 220 Ω^{-1}, i.e., approximately 10,000 times as much. At the same time, sulfuric acid in dioxan, as in water, forms a complex compound – the crystalline dioxanate [3, 4]. It was of interest to study the behavior of sulfuric acid in mixed aqueous dioxan solvent for varying ratios of dioxan to water. For this purpose, 0.1 N and 0.01 N solutions of sulfuric acid were prepared in aqueous dioxan mixtures having electrical constants equal to 12 and 37. If we add to these the well studied solutions of sulfuric acid in water and also solutions of sulfuric acid in dioxan [3], we obtain a series of solutions of sulfuric acid in media with the following dielectric constants: 2,28,12, 37 and 81.



Dependence of specific electrical conductivity of 0.1 N solutions of sulfuric acid in aqueous dioxan on temperature.

Aqueous dioxan solutions of sulfuric acid were prepared in graduated jars with ground-glass stoppers. They were both transparent and colorless like aqueous solutions of sulfuric acid and kept well. The results of the specific and equivalent electrical conductivity measurements for sulfuric acid in aqueous dioxan mixtures are given in Table 1.

As seen from the data in Table 1, at different concentrations and temperatures, specific electrical conductivity of aqueous dioxan solutions of sulfuric acid increases with increasing content of water in the system.

The specific electrical conductivity of solutions increases with increasing temperature, as may be concluded from Fig. 1. The curve for DC = 12 in the temperature range studied is represented by an ascending straight line; for DC = 37 the increase is more pronounced and not so even.

TABLE 1

Specific Electrical Conductivity of Aqueous Dioxan Solutions of Sulfuric Acid.

DC	H_2SO_4 concentration (N)	$\varkappa \cdot 10^3$						
		45°	40°	35°	30°	25°	20°	15°
12	0.1	0.7431	0.7311	0.7014	0.6671	0.6328	0.5982	0.5609
12	0.01	0.1108	0.1060	0.09811	0.09609	0.09156	0.08396	0.07816
37	0.1	6.901	6.639	6.561	6.393	5.184	4.618	4.412
37	0.01	0.7027	0.6311	0.5801	0.5373	0.4875	0.4267	0.3941

TABLE 2

Equivalent Electrical Conductivity of Aqueous Dioxan Solutions of Sulfuric Acid.

DC	Dilution	λ						
		45°	40°	35°	30°	25°	20°	15°
12	10	7.431	7.311	7.014	6.671	6.328	5.982	5.609
12	100	11.08	10.60	9.811	9.609	9.156	8.396	7.816
37	10	69.01	66.39	65.61	63.93	51.84	46.18	44.1
37	100	70.27	63.11	58.01	53.73	48.75	42.67	39.41

The results are no less interesting on comparing the values for the equivalent electrical conductivities of these solutions.

As seen from the data in Table 2, an increase in the relative water content is accompanied by an increase in equivalent electrical conductivity of aqueous dioxan solutions of sulfuric acid.

SUMMARY

1. Specific and equivalent electrical conductivity of solutions of sulfuric acid in aqueous dioxan mixtures with high dielectric constants 37 and 12, have been determined. The studies were carried out at the temperature range 15 to 45°, for each 5°.

2. It has been established that for different concentrations and the same temperature, the electrical conductivity of solutions is higher, the greater the amount of water contained in the aqueous dioxan solvent.

3. Electrical conductivity of the solutions increases with increasing temperature.

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STUDY OF REDISTRIBUTION OF HYDROGEN BETWEEN HYDROCARBONS ON ALUMINOSILICATE CATALYST USING CARBON ISOTOPE C^{14}

S. Z. Roginsky and T. I. Andrianova

In connection with results obtained in much earlier work [1], relating to a study of secondary cracking reactions of hydrocarbons using isotopic methods, the necessity arose to elucidate the possible role of redistribution of hydrogen between hydrocarbons of different unsaturation. The most direct way would be the use of deuterium or tritium. However, in view of the great mobility of hydrogen, it is difficult to avoid complications connected with isotopic exchange of hydrogen. We tried to overcome this difficulty by using radioactive carbon C^{14} in a study of hydrogen exchange between hydrocarbons.

An advantage of work with C^{14}, apart from the absence of a direct exchange, is the relatively simple method with a high sensitivity of radioactive analysis which permits detection of even a small exchange of hydrogen. In this work the results are given of a study, with the aid of C^{14}, of redistribution of hydrogen between ethylene and three paraffins: ethane, n-butane and n-octane.

The reaction was carried out in a continuous apparatus [1] at atmospheric pressure. A mixture of saturated and unsaturated hydrocarbons was made up in a gasometer and fed evenly through a graduated capillary, into a previously evacuated reactor containing synthetic aluminosilicate catalyst and heated to a definite temperature. After passing through the catalyst, the products were frozen in a trap with liquid nitrogen and then analyzed by chemical and radiometric methods. On using a labelled hydrocarbon under our reaction conditions, proceeding without change in the hydrocarbon skeleton, only hydrogenation of the olefin by the paraffin may be produced, this, in the case of mixtures of ethylene and ethane and ethylene and n-butane, being expressed by Equations (a) and (b)

$$H_3C-C^{14}H_3 + H_2C=CH_2 \rightleftharpoons H_2C=C^{14}H_2 + H_3C-CH_3, \qquad (a)$$

$$H_2C=C^{14}H_2 + n\text{-}C_4H_{10} \rightleftharpoons H_3C-C^{14}H_3 + n\text{-}C_4H_8. \qquad (b)$$

In such a redistribution of hydrogen, redistribution of radioactivity must proceed between the reaction components. In Equation (a), a molecule of radioactive ethane gives up two atoms of hydrogen to inactive ethylene and is itself converted to ethylene while retaining its own radioactivity and inactive ethylene is hydrogenated by hydrogen obtained from ethane and stays nonradioactive. As we know the general and specific radioactivity of the resulting ethane and ethylene and the radioactivity of the reaction products, the degree of approximation of the system to equilibrium, in which the C^{14} content in ethane and ethylene is the same, may be determined. In Equation (b), radioactive ethylene is hydrogenated by n-butane, the latter converting to butylene. Redistribution of hydrogen between ethylene and ethane, n-butylene and n-butane, etc., is not accompanied by a change in elementary chemical composition; therefore it must belong to the category of isotopic exchange reactions.

Insofar as distribution of C^{14} between two hydrocarbons varies in a reaction, then it seems that the isotopic exchange of carbon is connected with transfer of hydrogen. Examples of exchange of one element arising at the expense of transfer of atoms of another, is met fairly frequently in the chemistry of isotopes. We notice that redistribution of hydrogen between the olefin and paraffin with a different number of carbon atoms in the molecule, or with a different structure of the molecule, is an ordinary specific chemical reaction and does not lead to isotopic exchange of carbon.

The radioactivity of each of the reaction components was determined by combustion of a large portion of the gas in admixture with oxygen, over platinized asbestos, according to the similar method used in microanalysis, for carbon. Carbon dioxide produced on combustion of the hydrocarbon, was absorbed by an alcoholic solution of caustic soda and precipitated in the form of barium carbonate by treating with barium chloride solution. The barium carbonate precipitate was washed, dried, weighed and then made into a "target" on an aluminum disc and this was introduced into the chamber of a bell-type recorder. The number of impulses of the target and the radioactivity of a given fraction of barium carbonate were determined and consequently the radioactivity of the combusted part of the hydrogen. The method of radioactive analysis described in more detail in previous work [1], was chosen.

Redistribution of hydrogen between ethane, labelled C^{14} and nonlabelled ethylene was studied at 405 and 555° in mixtures containing 57.7 to 59.5 % ethane and 40.5 to 43.3% ethylene. Time of contact was 23.6-26.8 sec. The equilibrium exchange constant of carbon must be very close to unity; therefore the data for the radioactive analysis obtained by us, show that under the conditions of the investigation, equilibrium is not far from being reached. Redistribution of hydrogen according to Equation (a), detected according to radioactivity displayed in ethylene and according to general decrease in, and specific radioactivity of, ethane, does not exceed 5.2% calculated on the initial amount of ethane. Redistribution of hydrogen hardly varies at all with variation of temperature by 150°. An examination of the data relating to chemical analysis of the products and the radioactivity balance, show a deviation in the amount of ethane determined according to the chemical and radioactive analyses – according to the chemical analysis more ethane was formed than according to the radioactive analysis. The source of this formation of ethane may be hydrogenation of original inactive ethylene by coke, which, according to our data, is formed in preference from ethylene. Therefore it is assumed that a secondary reaction may take place according to the following:

Ethylene → coke

coke + ethylene → coke (poor in hydrogen) + ethane

Conversion of ethylene into ethane by "self-saturation", according to the scheme indicated, increases with increasing time of contact and for $\tau = 51.6$ sec. (at 506°) it reaches 19.7% calculated on the ethylene started with. It was also established that an appreciable part of the ethylene, from 5.9 to 10% is converted to coke which increases with increasing temperature and time of contact. Radiometry of the coke offered the possibility of estimating the radioactive ethane fraction in the formation of coke, this being shown to be not very large: only from 0.2 to 0.6% on the original ethane. From a comparison of the material yield of coke and its radiometry, we succeeded in establishing that formation of coke took place, for example, by 95%, calculated on the inactive ethylene and 5% on the radioactive ethane. In the system ethane–ethylene, ethane is represented as a hydrogen donor, in the hydrogen redistribution reaction; however, ethane is less capable of reaction in reactions taking place on aluminosilicate; therefore it was of interest to test the amount of donor hydrogen in reactions connected with hydrogen redistribution, rather than the reactive saturated hydrocarbons, in particular, n-butane and n-octane. A study of hydrogen redistribution in these systems was carried out at 405° for a decreasing role of secondary cracking.

Redistribution of hydrogen between ethylene, labelled C^{14} and inactive n-butane. The reaction was carried out at a temperature of 405°, time of contact 21 sec for mixtures containing 54.4% ethylene and 45.6% n-butane.

$$H_2C^{14}{=}CH_2 + C_4H_{10} \rightleftarrows H_3C^{14}{-}CH_3 + C_4H_8. \tag{c}$$

After passing through the layer of catalyst, the reaction products were frozen in a trap by liquid nitrogen, then separated in a micro-column which permitted carrying out a satisfactory separation of C_2 and C_4 fractions. Fraction C_4, after separation, was mixed with an excess of inactive ethylene and the mixture distilled repeatedly; in this way we succeeded in releasing the radioactive ethylene in fraction C_4, from the mixture. The radiometric data show that 13.4% of the radioactive ethylene is converted to ethane. A comparison of the material yield of ethane and its yield according to radioactivity, and also the fairly high activity of ethane, compels us to assume that in this case ethane is formed basically from ethylene; however, a much lower specific radioactivity than in the original ethylene and the higher yield of ethane determined chemically (17.4%) compared with the yield from ethylene measured radiometrically (13.4%), forces us to seek a secondary reaction for formation of ethane. In particular, this may be destructive alkylation:

$$H_2C^{14}=CH_2 + n\text{-}C_4H_{10} \rightleftarrows C^{14}C_3H_8 + C_2H_6 \qquad (d)$$

and also

$$C^{14}C_3H_8 + \text{coke} \rightarrow C^{14}C_3H_{10}.$$

Such an assumption agrees with the fact that fraction C_4, after passing through the catalyst, in admixture with radioactive ethylene, possessed radioactivity in an amount of 2.4% on the original radioactive ethylene. The presence of radioactivity in fraction C_4 may conceivably explain also reaction of ethylene with formation of butylene and its possible subsequent hydrogenation with hydrogen of coke, to butane, according to the equation:

$$2CC^{14}H_4 \rightleftarrows C^{14}C_3H_8. \qquad (e)$$

$$C^{14}C_3H_8 + \text{coke} \rightarrow C^{14}C_3H_{10}.$$

For the system ethylene, labelled C^{14} and inactive n-butane the possibility has been established of limiting the role of ethylene in direct redistribution of hydrogen with n-butane with formation of ethane and butylene and its part in self-saturation to ethane with separation of coke, since the resulting specific radioactivity in this and in other cases of ethane, is exactly the same. It does not help to use a labelled other component – n-butane. Here the use of a labelled hydrocarbon is desirable. The data obtained qualitatively show the direct hydrogenation of ethylene by butane proceeds slowly, since conversion of ethylene to ethane, amounts to only 13.4% calculated on the starting material; in this percent straight hydrogenation takes place as well as self-saturation of ethylene to ethane with formation of coke, which is identical with what has been established in previous tests on the reaction of ethylene with ethane. Quantitative determination of straight redistribution of hydrogen between olefin and paraffin, and self-saturation of the olefin via coke using isotopic C^{14} is possible in systems containing an equal number of carbon atoms, for example in the system butane–butylene, in which one of the hydrocarbons must be labelled. From radiometry of coke in this test, it follows that 2.6% of the original ethylene has been used up in forming coke. Comparisons of the material yield of coke and the yield according to radioactivity and also calculating the specific radioactivity, show that in mixtures of ethylene with n-butane, the role of the paraffin fraction in forming coke is greater than in mixtures of ethylene with ethane. Coke was formed on 74% of the radioactive ethylene and on 26% of the nonradioactive butane for approximately stoichiometric proportions of ethylene and butane in the mixture.

Redistribution of hydrogen between ethylene, labelled C^{14} and nonradioactive n-octane. The reaction was studied at a temperature of 405°. For the experiment 80 M Mole n-octane and 46.9 M Mole ethane were taken.

$$H_2C^{14}=CH_2 + C_8H_{18} \rightleftarrows H_3C^{14}-CH_3 + C_8H_{16}. \qquad (f)$$

Introduction of both components into the layer of catalyst was carried out simultaneously and uniformly. The time of contact was 9.4 sec. The reaction products, after leaving the reactor, were frozen in liquid air and then submitted to chemical and radiometric analysis. Rectification of the products was not carried out, as a control experiment established that at 405° cracking of n-octane on aluminosilicate is very low. In the gaseous part of the products, the content of unsaturated compounds was determined chemically. The saturated part was subjected to combustion and its radioactivity determined. The radioactivity of the unsaturated fraction was determined by difference.

As the experimental data show, saturated gases (among them ethane) are contained in the products in an amount comprising 23.8% of the original ethylene. Radiometry of the saturated gases showed that ethane formed from ethylene is only 12.3%, and the specific radioactivity of ethane, for example, is half the value of the specific radioactivity of the original ethylene. This indicates that the saturated gases are formed partly from ethylene and partly from n-octane, since combustion of the saturated gases showed that they contain, apart from ethane, also some hydrocarbons with a number of carbon atoms greater than 2, which therefore have evidently been formed by destructive alkylation of n-octane with ethylene according to a reaction of the type:

$$H_2C^{14}{=}CH_2 + C_8H_{18} \longrightarrow C_3H_8 + C^{14}C_6H_{14}. \qquad (g)$$

The presence of radioactivity in liquid products in an amount of 2.7% of the original radioactivity of the ethylene, confirms the possibility of such a reaction. In the system ethylene – n-octane, and also in the system ethylene–n butane, there is no limit to the role of the ethylene fraction in intermediate redistribution of hydrogen with n-octane (with formation of ethane) and the role of ethylene in self-saturation to ethane via coke. However, if we consider that both these processes lead to conversion of ethylene to ethane, only to the extent of 12.3% on the original amount, then it is obvious that the role of the fraction in redistribution of hydrogen with n-octane is also evidently small. Radiometry of coke showed that it contains 3.6% of the original radioactivity of ethylene. The specific radioactivity of coke in conjunction with its material yield permitted us to establish that it is formed in a yield of 47% on the ethylene and 53% on the n-octane. According to our data, there cannot be a quantitative comparison of the magnitude of redistribution of hydrogen between ethylene and saturated hydrocarbons with a different number of carbon atoms; however, qualitatively, the difference is not large.

The authors express their thanks to E. L. Raiskinoi for his part in the experimental work.

SUMMARY

1. With the aid of isotopic carbon C^{14} it is shown that straight redistribution of hydrogen between ethylene and paraffins – ethane, n-butane and n-octane – under cracking conditions, on aluminosilicate contacts, is not high.

2. It has been established that on interaction of an olefin with a saturated hydrocarbon on aluminosilicate, the olefin hydrogenation reaction to the paraffin with exactly the same number of carbon atoms, by hydrogen of coke, takes place to a greater extent than redistribution of hydrogen.

3. The use of C^{14} permits the quantitative determination of the ethylene and paraffin fraction with a different number of carbon atoms by the coke formation. With an increasing number of carbon atoms, the role of the paraffins in formation of coke also increases.

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STUDY OF THE MANNER OF HYDROGEN TRANSFER IN OXIDATION – REDUCTION REACTIONS

IX. LEIKART REACTION

A. F. Rekasheva and G. P. Miklukhin*

In the previous investigation of this series [1], it was shown that trimethylamine obtained from heavy ammonium chloride (ND_4Cl) and ordinary formaldehyde, does not contain an excess of deuterium in the C–H links, i.e., reduction of one molecule of aldehyde takes place at the expense of hydrogen atoms of a different C–H link since a transferred atom of hydrogen does not interact with a mobile hydrogen (for example, an N–D link) of the medium. Thus, with reference to the source and the manner of the hydrogen, reductive methylation is similar to the Cannizzaro reaction [2], reducing aldehydes to alcohols [3], and a number of other oxidation–reduction reactions [4].

Determination of the difference in the rate of transfer of hydrogen and deuterium (isotopic effect) in many cases gives valuable indications of the mechanism of the reaction connected with different X–H links [5]. There was considerable interest in elucidating the extension of the analogy in the mechanism of oxidation–reduction reactions and factors of interest to us which define the magnitude and possibility of determining the isotopic effect experimentally.

We studied the reaction of formation of amines from carboxylic compounds and ammonium formate (Leikart reaction), the mechanism of which is in agreement with existing assumptions and approximate re-ductive methylation.

Carrying out the Leikart reaction with ammonium formate containing deuterium in C–H linkages, may give data on the origin of the hydrogen which is transferred to the carbon of the carbonyl compound and the manner of its transfer, as well as the isotope effect in this reaction if reduction takes place at the expense of the hydrogen of the C–H links without interaction with the medium.

We studied formation of α-phenylethylamine and benzylamine from acetophenone and benzaldehyde, respectively, on heating them with $DCOONH_4$, according to the method described [6, 7], the only difference being that for economy of the deuterium compound, in place of 5-6 times the excess of $DCOONH_4$, 2-3 times the excess was introduced into the reaction. As a result of this, our yields of amines were lower than those given in the literature. We prepared heavy ammonium formate by decomposition of oxalic acid in presence of glycerine and heavy water. 1 mole anhydrous oxalic acid was heated on a sand bath for 15-17 hours with 0.5 mole glycerine and 1 mole D_2O (~ 80%) to 115-125°. The resulting water and formic acid were distilled off and the temperature of the mixture was raised to 175°. The distillate was placed in a distilling flask and redistilled. 55 ml ordinary water was added to the residue and the distillation continued. All the distillates which contained heavy formic acid, DCOOD, were collected together. Repeated distillations were carried out with the object of attaining complete hydrolysis of the formic acid ester of glycerine, formed by decarboxylation of the oxalic ester. Formic acid was precipitated from the distillate in the form of its lead salt by adding finely powdered lead carbonate. The lead formate was recrystallized from water and decomposed with a solution of ammonium carbonate. The precipitated lead carbonate was filtered off and the solution of ammonium formate evaporated, first on the water bath, then in a vacuum desiccator over caustic soda. The ammonium formate obtained melted at 124° after drying.

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* Deceased.

The amounts of substances taken, yields of amines, excess deuterium content in them and in the original $DCOONH_4$, are given in the table.

Production of α-Phenylethylamine and Benzylamine from Acetophenone, Benzaldehyde and NH_4OOCD

Experiment No.	Excess deuterium (in γ)						Molar ratio	Yield of amine, (%)	% of deuterium transferred to amine	Average $\frac{k_H}{k_D}$
	Found in C−H of original NH_4OOCD	Found in H_2O from amine combustion	Found in H_2O from semicarbazone combustion	Calc. in CH_3 group of acetophenone	Calc. in CH− links of amine	Found in H_2O from reaction mixture	$\frac{NH_4OOCD}{R'-\underset{O}{\underset{\|}{C}}-R''}$			
	1	2	3	4	5	6	7	8	9	10
Yield of α-Phenylethylamine										
1	7350	429	—	187	4990	—	3 : 1	37	67.7	—
2	7350	402	—	187	4654	—	3 : 1	34	63.5	—
3	7350	421	—	187	4900	—	3 : 1	41	66.6	—
4	7350	410	63	231	4640	—	2.1 : 1	37	63.2	—
5	6600	365	56	209	4130	27	1.5 : 1	28	62.6	—
6	6600	330	45	165	3795	—	1.5 : 1	21	57.5	—
7	6600	375	45	165	4380	24	1.5 : 1	20	66.5	—
								Average	**64.0**	**1.56**
Yield of benzylamine										
8	6600	525	—	—	4725	110	4 : 1	20	71.6	—
9	6600	498	4	—	4480	55	3.2 : 1	23	68.0	—
10	6600	440	0	—	3960	58	3.4 : 1	21	60.0	—
11	6600	480	19	—	4320	81	3.8 : 1	22	65.5	—
								Average	**66.3**	**1.51**

α-Phenylethylamine (m. p. 184-186°), after distillation, was precipitated and recrystallized from water in the form of the oxalate, which was decomposed over copper oxide to determine the deuterium content of the amine from the density of the water after combustion.

Benzylamine was purified by distillation in vacuo (b. p. 180-182° at 680 mm) and decomposed in the form of the free base. In both cases the deuterium from the N−H and O−H linkages was washed out by decomposing with ordinary water. On calculating the isotope content of the water in the amines, there should be taken into consideration the fact that deuterium linked with the α-atom of the carbon of α-phenylethylamine, on decomposition of its oxalate with 13 times the amount of hydrogen of ordinary isotopic composition, is diverted from the residual position of the molecule, deuterium entering into the side chain of benzylamine being diluted 9 times by combustion.

From the data given in the table, it is seen that α-phenylethylamine, as well as benzylamine, contains a marked excess of deuterium in the C−H links. It follows from this that reduction takes place at the expense of hydrogen of the C−H links, the transferred hydrogen not being exchanged with hydrogen of N−H and O−H links of the medium. In a more accurate determination of the magnitude of the isotopic effect and its elucidation, there do not arise (with sufficiently rigid conditions of carrying out the process, i.e., heating at 180-190° for a period of 1.5-3 hours) the ordinary exchange reactions; we isolated from the reaction mixture not only amines, but also water which had been formed, and also unreacted carbonyl compounds, and determined their isotope content.

Water and carbonyl (in form of acetone or benzaldehyde) were distilled off from the reaction mixture and separated in a separating funnel. The ketone (or aldehyde) was dried, distilled with a dephlegmator and precipitated from alcoholic solution in the form of the semicarbazone. The semicarbazone obtained was recrystallized from ethyl alcohol (melting points of semicarbazones: acetophenone 203°, benzaldehyde 220-222°). The semicarbazones, after careful drying in vacuo, were burnt over copper oxide. The isotope content of the water was determined after combustion from its excess density.

Water from the reaction mixture, after separation of the carbonyl compound from it, was repeatedly extracted with absolute ether. The ether was dissolved in water, removed or boiled off on the water bath or treated with paraffin while heating. The water was further purified by the usual method for analysis of isotopes. The data on the isotope composition of water and acetophenone and benzaldehyde semicarbazones, given in the Graph 6 and in the 3 tables, point to the fact that water, as well as unreacted acetophenone, contain only a slightly excessive amount of deuterium. Deuterium has taken practically no root at all in benzaldehyde. The excessive density of water, on combustion of acetophenone, corresponds to a deuterium content of 165-230 γ in its methyl group, which is a much higher deuterium content in the water from the reaction mixture. The mechanism of deuterium introduction into acetophenone under the Leikart reaction conditions is not clear. On calculating the percentage deuterium transfer into α-phenylethylamine, the deuterium content of its tertiary carbon atom is decreased by an amount corresponding to the amount of deuterium in acetophenone. The calculations were carried out according to the following formula:

$$X = 13\left(A - \frac{B \cdot 11}{13}\right),$$

where A is the excessive density of water from combustion of α-phenylethylamine oxalate, B is the excessive density of water from combustion of the semicarbazone of acetophenone from the reaction mixture. For Experiment 4, for example, the formula takes the following form:

$$X = \left(410 - \frac{63 \cdot 11}{13}\right) \cdot 13 = 5330 - 693 = 4647 \sim 4650\,\gamma.$$

The values of X obtained by such a calculation are given in Graph 5 of the table. For Experiments 1-3, in which the deuterium content of acetophenone was not determined from the reaction medium, the average value of B was taken as 25 γ.

A comparison of the amounts of deuterium in hydrogen linked with the α-carbon atom of amines containing deuterium in the C−H links of the original ammonium formate shows that in amines, hydrogen is transferred to the C−H links of NH_4OOCH. The percent transfer of deuterium in amines reaches 60-70, i.e., the reaction proceeds with a low isotopic effect $\frac{K_H}{K_D}$ = 1.5-1.6 .*

The data obtained indicate that the amination reaction of carbonyl compounds by ammonium formate is another example of oxidation−reduction interaction for which direct transfer of hydrogen is observed from the reducing carbon to the reduced compound without exchange with mobile hydrogen of the medium. The isotopic effect of the reaction is low; consequently, with reference to the origin and manner of transfer of hydrogen, as well as with reference to the magnitude of the isotopic effect of the Leikart reaction it approximates the Cannizaro reaction [8] which supports the assumption of similar mechanisms of both processes.

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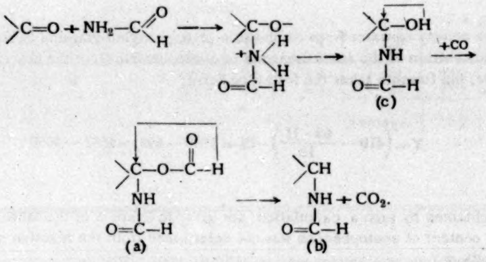
* We calculated the magnitude of the isotopic effect by a simple division of the deuterium content of the reaction product by the deuterium content of the original salt, in view of the fact that only a small part of it is used in forming the amine and there is always an excess of salt present in mixtures.

With regard to the mechanism of the Leikart reaction, a study entailing a great deal of work [9] contains not a single reference to it in the literature. Our data do not permit us to give a single known result in support of one of them; however, the mechanisms which suggest the possibility of introduction into the reaction products of mobile hydrogen of the medium must be rejected on the basis of data obtained with the aid of the isotope method. For example, Metai suggested that formation of benzylamine from benzaldehyde and formamide [9], is expressed by the equations:

$$C_6H_5CHO + 2HCONH_2 \rightarrow C_6H_5CH(NHCHO)_2 + H_2O,$$
$$C_6H_5CH(NHCHO)_2 \rightarrow C_6H_5CH{=}NCHO + HCONH_2,$$
$$HCONH_2 + H_2O \rightarrow HCOONH_4 \rightarrow HCOOH + NH_3,$$
$$HCOOH \rightarrow H_2 + CO_2;\ HCOOH \rightarrow H_2O + CO,$$
$$C_6H_5CH{=}NCHO + H_2O \rightarrow C_6H_5CH_2N(OH)CHO \xrightarrow{+H_2}$$
$$\longrightarrow C_6H_5CH_2NH_2 \cdot HCOOH \longrightarrow C_6H_5CH_2NHCHO.$$

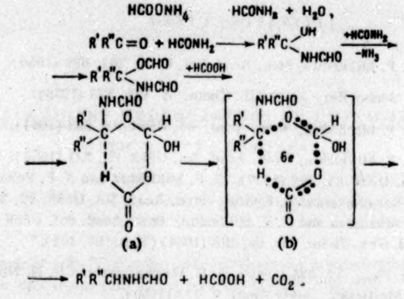
In agreement with this, an atom of hydrogen formed from water arising on decomposition of formic acid, passes to the hydrogen atom of the side chain of an unsaturated intermediate compound, which conforms with the data obtained by us. Mousseron and colleagues [10], consider that reduction in the Leikart reaction takes place by carbon monoxide and not formic acid, and suggest the following mechanism of interaction of carbonyl compounds with unsubstituted formamide:



It is easy to see that hydrogen, transferred to the carbon chain on conversion of (a) to (b), not depending on the manner of its transfer, must also have an isotope content which enters into the composition of the hydroxyl group in the hydrogen of the solvent as well as in compound (c). Our data also permit rejection of this mechanism.

Acid catalysis (at a definite pH range [11]), has been established for the Leikart reaction. This fact is explained well if we take into consideration that a state of reduction precedes formation of an intermediate compound of the ether type and take into account that in the work [12], acid catalysis is shown for disproportionation of ethers of various alcohols.

On the basis of data in the literature and data obtained in this and previous work, we consider that the Leikart reaction very probably proceeds according to the following mechanism:



We do not insist on details of this mechanism. In place of formamide, a stable ammonium salt or formic acid, etc., may also take part. We consider formation of an intermediate compound of type (a) obligatory, this being decomposed to reaction products via a reaction complex similar to (b).

In the reaction complex (b), 6 electrons are located in field 6 of the nucleus. In agreement with the preceding, the reaction procedure developed by Ya. K. Syrkin [13], via similar formations lowers the activation energy and therefore the numerous processes take place in exactly the same way. E. A. Shilov in 1941 [14], has already indicated the important role which such intermediate compounds play. It might be thought that the mechanism examined excludes an explanation of the question as to whether hydrogen is transferred in the form of atoms or ions in the reaction process.[*] Conversions (a) and (b) proceed by rapid transfer of electrons, as a result of which the atoms of the nucleus are drawn together. A macro picture of the transfer corresponds absolutely to homolysis and not to heterolysis.

SUMMARY

1. Using the formation of α-phenylethylamine and benzylamine from acetophenone and benzaldehyde as an example, the mechanism of formation of amines from carbonyl compounds and ammonium formate (Leikart reaction), has been studied with the aid of deuterium.

2. It has been established that, on carrying out a reaction with heavy ammonium formate $DCOONH_4$, hydrogen passes to the carbonyl atom of the aldehyde (or ketone) from the C−D link of the formate. The hydrogen substituted does not take part in the isotopic exchange reaction with the easily exchanged hydrogen of the medium.

3. The ratio of the rate of exchange of hydrogen and deuterium (kinetic isotopic effect) for formation of α-phenylethylamine and benzylamine has been found to be equal to 1.5-1.6.

Thus, with reference to the principles and methods of hydrogen transfer as well as with respect to the magnitude of the isotopic effect, the Leikart reaction is similar to the Cannizzaro reaction which deals with the benefit of the mechanism of hydrogen transfer in these reactions (intramolecular transfer of hydrogen in complexes formed from reactive compounds).

4. The data obtained permit rejection of the mechanisms of the Leikart reaction which assume that by the hydrogen produced, the C−H links of the amines are reformed, being expressed as water or hydroxyl groups of other compounds formed during the course of the reaction.

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[*] We thank A. I. Brodsky and A. I. Kipriyanoi for criticism of our earlier ideas.

5. A probable mechanism of the Leikart reaction is suggested.

6. Syntheses of heavy formic acid DCOOD and its ammonium salt, are described.

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* T. p. = C. B. Translation pagination.

OXIDATION OF ALKADIENE HYDROCARBONS OF UNSYMMETRICAL STRUCTURE WITH ACETYL PEROXIDE. II

V. I. Pansevich-Kolyada

We established in previous work [1] that dioxides and oxidodiol monoacetates were formed by oxidation of unsymmetrical 1, 3-diene hydrocarbons with acetyl peroxide in ether at 20-25°.

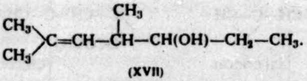
In this investigation we tried to ascertain the most probable mechanism for this extremely interesting reaction and to examine, as well, the effect of a series of factors on its course. For this purpose four more hydrocarbons were oxidized under the conditions described earlier [1]: 2,4-dimethylpentadiene-2,4, 2,4-dimethylheptadiene-2,4, 2,4,5-trimethylhexadiene-2,4 and 2,4-dimethyldecadiene-2,4 (Table 1) allowing 2 moles of peroxide to 1 mole of hydrocarbon. Furthermore, 2,4-dimethylhexadiene-2,4 and 2,4-dimethylheptadiene-2,4 were oxidized with 1 mole of peroxide for each mole of hydrocarbon.

In all cases, as in the previous work [1], , two reaction products, dioxides and oxidodiol monoacetates (Tables 2 and 3), were obtained by oxidizing 1 mole of hydrocarbon with two moles of peroxide. Different solvents (ether and acetic acid), changes in temperature(0, 25°), and the mixing order of hydrocarbons with peroxide did not substantially affect the course of the reaction.

It should also be noted that the hydrocarbons 2,4-dimethylpentadiene-2,4 and 2,4,5-trimethylhexadiene-2,4 cannot have cis- and trans- isomers, while 2,4-dimethylpentadiene-2,4 cannot have an isomer at the double bond. Thus, the formation of the two products could not have been due to structural or stereochemical isomerism of the original hydrocarbons [2].

Two reaction products — unsaturated monoxides (XII, XV) and monoacetates of unsaturated glycols (XIII, XVI) — were also obtained by oxidizing 1 mole of 2,4-dimethylhexadiene-2,4 and 2,4-dimethylheptadiene-2,4 with 1 mole of peroxide.

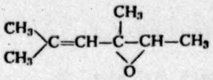
The monoxide (XV), obtained by oxidizing 2,4-dimethylheptadiene-2,4, was hydrogenated over Raney nickel to determine its structure and, consequently, the order of oxidation of the double bonds. The hydrogen combined at room temperature when the oxide ring was opened and the double bond preserved. The alcohol obtained was distilled at ordinary pressure without decomposition [3, 4] and in contrast to alcohols with double bonds in the allyl position, did not undergo esterification in the presence of sulfuric acid [5]. From these properties, the following formula may be ascribed to it (XVII):

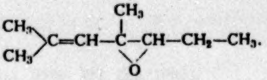


$$(CH_3)_2C{=}CH{-}\overset{CH_3}{\overset{|}{CH}}{-}CH(OH){-}CH_2{-}CH_3.$$

(XVII)

This alcohol structure agrees with known facts on the opening of the oxide ring by hydrogenation of unsaturated α-oxides on the vinyl side of the double bond [6-8] and, apparently, the unsaturated monoxide structures could be expressed by the formulas (XII, XV):

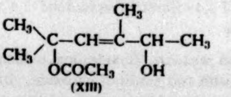

(XII)

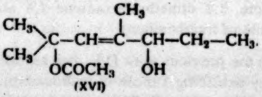

(XV)

Consequently, the acetyl peroxide oxidation of the hydrocarbons, investigated by us, began, apparently, at the second bond in the 4,5 position.

The unsaturated monoxide – 2,4-dimethyl-oxido-4,5-heptane-2 (XV) was oxidized by acetyl peroxide. The only reaction product was the dioxide 2,4-dimethyl-dioxido-2,3-4,5-heptane (II) which we also obtained by oxidizing 2,4-dimethylheptadiene-2,4 with two moles of peroxide. In this case no monoacetyl derivatives were formed. Hence, dioxides do not precede or serve as the starting material for the formation of oxidodiol monoacetates during the oxidation of 1,3-diene hydrocarbons with acetyl peroxide.

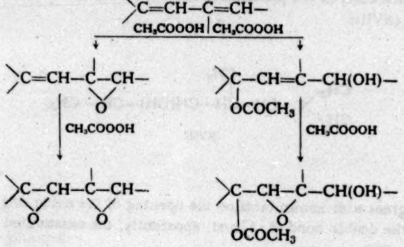
The unsaturated glycol monoacetates (XIII, XVI) as well as their saponification products, the glycols, were oxidized by lead tetraacetate. No acetaldehyde, propionaldehyde or acetone was found among the oxidation products [1]. This indicates that the monoacetates do not have adjacent oxidized carbon atoms and that their structure may be represented by the formulas (XIII, XVI):


(XIII)


(XVI)

Materials of this structure could have been formed by the addition of the peroxide elements to 1,3-diene hydrocarbons in the 1,4 position. The oxidodiol monoacetates could then be formed by further oxidation of the unsaturated glycol monoacetates by the peroxide. Actually, the same oxidodiol monoacetate – 2,4-dimethyl-2-acetoxy-oxido-3,4-heptanol-5 (VI), was obtained by oxidizing the unsaturated glycol monoacetate – 2,4-dimethyl-2-acetoxyhepten-2-ol-5 (XVI), with 1 mole of peroxide as the one obtained by oxidizing 2,4-dimethylheptadiene-2,4 with 2 moles of peroxide.

Thus, apparently, the oxidation of the 1,3-diene hydrocarbons, investigated by us, with acetyl peroxide proceeds in two ways simultaneously – in the 1,2 and 3,4 positions with the formation of dioxides and in the 1,4 and 2,3 position with the formation of oxidodiol monoacetyl derivatives according to the following scheme:



Such a reaction between acetyl peroxide and 1,3-diene hydrocarbons is possibly affected not only by the nature of the hydrocarbons but also by that of the peroxide, which, as has been established by the work of N. M. Emanuel [9], may be found in two interconvertable forms.

EXPERIMENTAL

Oxidation of Hydrocarbons with a Double Quantity of Acetyl Peroxide

The hydrocarbons were prepared by treating mesityl oxide with an alkylmagnesium halide to give the appropriate unsaturated tertiary alcohol, which was dehydrated by boiling with $MgSO_4$ or Na_2SO_4 (Table 1).

TABLE 1

Characteristics of the Hydrocarbons.

No.	Name of hydrocarbon	Boiling point	n_D^{20}	d_4^{20}	MR_D		Literature
					found	calculated	
1	2,4-dimethylpentadiene-2,4	91-92.0° (742 mm)	1.4400	0.7342	34.39	33.59	[4, 10, 12, 13]
2	2,4-dimethylhexadiene-2,4	115-117 (746 mm)	1.4435	0.7629	38.26	38.21	[1, 3, 4]
3	2,4-dimethylheptadiene-2,4	138-141 (738 mm)	1.4488	0.7644	43.50	42.83	[3, 4]
4	2,4,5-trimethylhexadiene-2,4	39-41 (13 mm)	1.4461	0.7732	42.77	42.83	[11]
5	2,4-dimethyldecadiene-2,4	88 (3 mm)	1.4521	0.7884	56.80	56.68	

The hydrocarbons were oxidized with the calculated quantity (73-91 %) of acetyl peroxide in twice the volume (to hydrocarbon) of dry ether. The oxidation continued for 5 to 10 days. The completion of the reaction was established by the iodometric method [1].

In the case of 2,4-dimethylhexadiene-2,4, the oxidation was also carried out in glacial acetic acid and in ether with the reverse order of addition of the reagents (the hydrocarbon was added to the peroxide solution); the same products were separated in these cases (X and XI; see Tables 2 and 3).

After neutralizing the acetic acid with soda, the reaction products were extracted with ether, dried with $MgSO_4$ and distilled in vacuum. For all the hydrocarbons two materials were obtained – dioxides and oxidodiol (glycol oxide) monoacetates.

The dioxides (I, II, III and IV) were colorless, mobile, pleasant-smelling liquids; they dissolved in cold water and organic solvents, quickly decolorized 1% potassium permanganate solution and liberated iodine from an aqueous potassium iodide solution [14, 15]. Their physical constants and analytical data are given in Table 2.

The oxidodiol monoacetates were colorless, glycerin-like liquids, with faint smells; they dissolved readily in cold water and organic solvents. The aqueous solutions had an acid reaction, apparently due to their hydrolysis. They quickly decolorized 1% $KMnO_4$ solution and liberated iodine from aqueous potassium iodide solution. They contained active hydrogen. Their physical constants and analytical data are given in Table 3.

Of all the dioxides and monoacetates obtained, the materials (IV) and (VIII) were difficultly soluble in water and the monoacetate (VIII) was unstable and partly decomposed on distillation, which also showed in its analytical data. However, the properties of this material's condensation product with acetic anhydride confirmed its structure.

Reaction of oxidodiol monoacetate (VIII) with acetic anhydride. 31.4 g of the material was heated for 6 hours on a water bath with twice the quantity of acetic anhydride, and then was boiled for 7 hours. The acetic anhydride was distilled off in vacuum. By distillation of reaction products, 6 g of material was isolated. This was a glycerin-like liquid with a faint smell, which liberated iodine from aqueous potassium iodide solution and was oxidized by 1% $KMnO_4$ solution. It did not contain active hydrogen. The analytical data corresponded to 2,4-dimethyl-2,5-diacetoxy-oxido-3,4-decane (IX).

TABLE 2

Characteristics of the Dioxides Obtained.

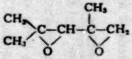
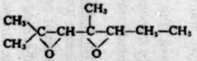
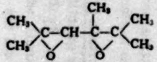
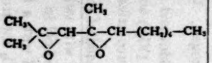
Name of dioxide and formula	Hydrocarbon oxidized (in g)	Dioxide obtained (in g)	Boiling point	n_D^{20}	d_4^{20}	MR_D		Elementary composition				Molecular weight	
								Found		Calculated			
						Found	Calculated	C	H	C	H	Found	Calculated
2,4-dimethyl-dioxido-1,2-3,4-pentane (I) 	46	11	64—67° (14 mm)	1.4213	0.9668	33.59	33.67	65.04, 65.27	9.68, 9.69	65.62	9.38	—	—
2,4-dimethyl-dioxido-2,3-4,5-pentane (II) 	40	8	64—66 (4.5 mm)	1.4320	0.9472	42.72	42.91	69.26	10.46	69.23	10.34	152.4, 148.5	156.0
2,4,5-trimethyl-dioxido-2,3-4,5-hexane (III) 	70	17	78.5—80 (9 mm)	1.4325	0.9497	42.74	42.91	68.44, 68.97	10.23, 10.36	69.23	10.25	141.2, 140.4	156.0
2,4-dimethyl-dioxido-2,3-4,5-decane (IV) 	95.5	22	105—107 (3 mm)	1.4412	0.9155	57.02	56.76	72.40	11.60	72.72	11.11	197.4	198.0

TABLE 2 (continued)

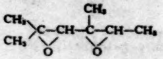
Name of dioxide and formula	Hydrocarbon oxidized (in g)	Dioxide obtained (in g)	Boiling point	n_D^{20}	d_4^{20}	MR_D		Elementary composition				Molecular weight	
								Found		Calculated			
						Found	Calculated	C	H	C	H	Found	Calculated
2,4-dimethyl-dioxido-2,3-4,5-hexane (X) 	—	—	52—55 (3 mm)	1.4229	0.9657	37.43	38.29	—	—	—	—	—	—
			55—57 (4 mm)	1.4250	0.9631	37.70	38.29	—	—	—	—	—	—

TABLE 3
Characteristics of Oxidodiol Monoacetates Obtained

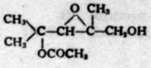
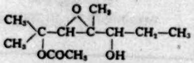
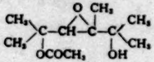
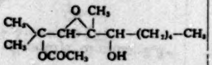
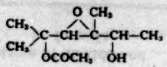
Name of monoacetate and formula	Hydrocarbon oxidized (in g)	Monoacetate obtained (in g)	Boiling point	n_D^{20}	d_4^{20}	MR_D		Elementary composition						Molecular weight	
								Found			Calculated				
						Found	Calculated	C	H	OH	C	H	OH	Found	Calculated
2,4-dimethyl-2-acetoxy-oxido-3,4-pentanol-5 (V) 	46	21	109—112° (8 mm)	1.4414	1.0635	46.72	46.51	57.34	8.80	—	57.44	8.51	—	—	—

TABLE 3 (continued)

Name of monoacetate and formula	Hydrocarbon oxidized (in g)	Monoacetate obtained (in g)	Boiling point	n_D^{20}	d_4^{20}	MR_D		Elementary composition						Molecular weight	
								Found			Calculated				
						Found	Calculated	C	H	OH	C	H	OH	Found	Calculated
2,4-dimethyl-2-acetoxy-oxido-3,4-heptanol-5(VI) 	40	19.5	120—125° (4 mm)	1.4475	1.0361	55.77	55.75	61.67	9.67	8.76	61.11	9.25	7.87	206.5	216
2,4,5-trimethyl-2-acetoxy-oxido-3,4-hexanol (VII) 	70	34.5	120—123 (9mm)	1.4490	1.0435	55.52	55.75	61.00	9.41	7.79	61.11	9.25	7.87	195.6, 202.0	216
2,4-dimethyl-2-acetoxy-oxido-3,4-decanol-5(VIII) 	95.5	51.5	126—128 (3 mm)	1.4543	0.9911	70.36	69.6	66.34, 66.28	10.97, 10.60	8.95, 8.78	65.10	10.07	6.50	207.7, 230.6	258
2,4-dimethyl-2-acetoxy-oxido-3,4-hexanol-5 (XI) 	—	—	99—101 (3 mm)	1.4460	1.0583	50.90	51.13	—	—	—	—	—	—	—	—

B. p. 140.5-145° (3 mm), n_D^{20} 1.4481, d_4^{20} 1.0000, MR_D 80.30; Calc. 78.90.

Found %: C 64.40, 64.10; H 9.90, 9.47. M 288.4, 290.2. $C_{16}H_{28}O_5$. Calculated %: C 64.00; H 9.30. M 300.

Oxidation of Hydrocarbons with Acetyl Peroxide in the Ratio of 1 Mole of Hydrocarbon : 1 Mole of Peroxide

1. Oxidation of 2,4-dimethylhexadiene-2,4. 48 g of 73.8% peroxide was added to 50 g of hydrocarbon in 140 ml of ether at 20-25°. The oxidation was quickly completed. After 2 days the reaction products were worked up as in previous experiments. By distilling them, two materials were obtained. One possessed an ester-like smell, was readily oxidized by permanganate, liberated iodine from an acetic acid solution of potassium iodide and did not contain active hydrogen. The analytical data was close to that of the unsaturated monoxide 2,4-dimethyl-oxido-4,5-hexane-2 (XII).

B. p. 137-139° (746 mm), n_D^{20} 1.4310, d_4^{20} 0.8500, MR_D 38.05; Calc. 38.25.

Found %: C 74.91, 74.66; H 11.14, 11.12. M 112.4, 113. $C_8H_{14}O$. Calculated %: C 76.19; H 11.11. M 126.

Repeated attempts to improve the analytical results were unsuccessful, apparently, because the monoxide was changed during the distillations.

The second material was a colorless, oily liquid which smelled like yarrow. It was immediately oxidized by 1% $KMnO_4$ solution and contained active hydrogen. It was the unsaturated glycol monoacetate – 2,4-dimethyl-2-acetoxyhexen-3-ol-5 (XIII).

B. p. 95-98° (8 mm), n_D^{20} 1.4560, d_4^{20} 0.9874, MR_D 51.23; Calc. 51.09.

Found %: C 64.27; H 9.76; OH 9.39. M 185. $C_{10}H_{18}O_3$. Calculated %: C 64.51; H 9.67; OH 9.14. M 186.

Analogous results were obtained on oxidizing 2,4-dimethylhexadiene-2,4 in ether at 0° and in glacial acetic acid.

Oxidation of the unsaturated glycol monoacetate (XIII) with lead tetraacetate. 18.8 g of 90% lead tetraacetate was added to 7.1 g of material in 25 ml of glacial acetic acid. Evolution of heat was not observed, in contrast to the oxidation of glycol oxide monoacetate by the same oxidizing agent [1]. The mixture was heated to 50-55° on a water bath. The volatile oxidation products were removed with a stream of CO_2 and trapped in 2,4-dinitrophenylhydrazine solution. 2,4-Dinitrophenylhydrazone fractions melting at 124-130° and 139-140° were obtained in small quantities, which were insufficient for determining the nature of the carbonyl compounds, from which they were derived. A sample of these hydrazones mixed with acetone 2,4-dinitrophenylhydrazone melted at 105-110°.

After neutralization of acetic acid with soda, the involatile oxidation products were extracted with ether. Upon distillation, the product of acetylation of the monoacetate (XIII) was apparently isolated – 2,4-dimethyl-2,5-diacetoxyhexene-3 (XIV).

B. p. 119-121° (10 mm), n_D^{20} 1.4480, d_4^{20} 1.0057, MR_D 60.69; Calc. 60.46.

Found %: C 62.70, 62.49; H 9.23, 8.93. $C_{12}H_{20}O_4$. Calculated %: C 63.15; H 8.77.

2. Oxidation of 2,4-dimethylheptadiene-2,4. 24 g of 80% acetyl peroxide was added to 30 g of hydrocarbon in 60 ml of ether at 20-25°. The oxidation was complete by next day. Two materials were obtained.

1) 2,4-Dimethyl-oxido-4,5-heptene-2 (XV) – a mobile, colorless liquid with a flower-like smell. It quickly decolorized permanganate solution, liberated iodine from an acetic acid solution of potassium iodide and did not contain active hydrogen.

B. p. 38-42° (4 mm), n_D^{20} 1.4338, d_4^{20} 0.8413, MR_D 43.32; Calc. 42.87.

Found %: C 76.54; H 11.47. M 143.4, 142.2. $C_9H_{16}O$. Calculated %: C 77.14; H 11.42. M 140.

2) 2,4-Dimethyl-2-acetoxy-hepten-3-ol-5 (XVI) – an oily, colorless liquid with a faint smell. It readily decolorized permanganate solution and contained active hydrogen.

B. p. 106-107° (4 mm), n_D^{20} 1.4515, d_4^{20} 0.9781, MR_D 55.11; Calc. 55.71.

Found %: C 65.01, 64.80; H 10.08, 9.97; OH 8.52, 8.70. M 208.5, 207.4. $C_{11}H_{20}O_3$. Calculated %: C 66.00; H 10.00; OH 8.50. M 200.0.

Hydrogenation of unsaturated monoxide (XV). 1.5 g of Raney nickel was added to 12.2 g of material dissolved in 50 ml of ethyl alcohol. Hydrogen was added with constant shaking at room temperature. Over 24 hours, 2020 ml of hydrogen was taken up; the calculated amount was 1998 ml. The nickel was filtered off, the ethyl alcohol was distilled off in vacuum, and then the reaction products were distilled. 7 g of a mobile, colorless liquid with a pleasant smell was obtained. The material decolorized 1% permanganate solution, added bromine and contained active hydrogen.

B. p. 54.5-55° (5 mm), n_D^{20} 1.4400, d_4^{20} 0.8417, MR_D 44.46; Calc. 44.82.

Found %: C 75.54, 75.79; H 12.96, 12.98; OH 10.98. M 139.6, 146.2. $C_9H_{18}O$. Calculated %: C 76.05; H 12.67; OH 11.97. M 142.

The alcohol obtained – 2,4-dimethylhepten-2-ol-5 (XVII) distilled without decomposition at 168° (732 mm) and was not esterified by methyl alcohol in the presence of a dilute solution of sulfuric acid [5].

Oxidation of unsaturated monoxide (XV) with acetyl peroxide. 11 g of 91.7% peroxide was gradually added to 14 g of monoxide in dry ether at 20-25°. The oxidation proceeded energetically. The reaction products were worked up by the usual method. By distilling them in vacuum, 4.5 g of material was isolated.

B. p. 64-66° (4.5 mm), n_D^{20} 1.4301, d_4^{20} 0.9415, MR_D 42.81; Calc. 42.91.

The data obtained correspond to the dioxide (II).

It should be noted that in the oxidation of the monoxide with acetyl peroxide, the oxidodiol monoacetate (VI) was not obtained at all.

Hydrolysis of the unsaturated glycol monoacetate (XVI). 40 ml of 5% aqueous NaOH solution was added to 8.4 g of material. The mixture was heated for 4 hours on a boiling water bath. The reaction products were extracted with ether, dried with $MgSO_4$ and distilled in vacuum. We isolated 3 g of an oily, colorless liquid, which contained active hydrogen and was readily oxidized by 1% permanganate solution.

B. p. 89-91° (2 mm), n_D^{20} 1.4679, d_4^{20} 0.9547, MR_D 46.04; Calc. 46.34.

Found %: C 68.08; H 11.92; OH 18.39. $C_9H_{18}O_2$. Calculated %: C 68.35; H 11.44; OH 21.5.

The data obtained correspond to 2,4-dimethylhepten-3-diol-2,5 (XVIII).

Oxidation of 2,4-dimethyl-2-acetoxyhepten-2-ol-5 (XVI) with acetyl peroxide. 4 g of 88% peroxide was added to 9.2 g of material (XVI) in twice the amount of ether. After 4 days the oxidation products were worked up in the usual way. On distillation in vacuum we isolated 5.5 g of a glycerin-like, colorless liquid, which was the oxidodiol monoacetate (VI).

B. p. 107-109° (2 mm), n_D^{20} 1.4474, d_4^{20} 1.0347, MR_D 55.81; Calc. 55.75.

SUMMARY

1. By acetyl peroxide oxidation of 2,4-dimethylpentadiene-2,4, 2,4-dimethylheptadiene-2,4, 2,4,5-trimethylhexadiene-2,4 and 2,4-dimethyldecadiene-2,4 in ether at 20-25° and 2,4-dimethylhexadiene-2,4 also in glacial acetic acid at 20-25° (with 2 moles of peroxide to 1 mole of hydrocarbon), dioxides and oxidodiol monoacetates were obtained in all cases.

2. By acetyl peroxide oxidation of 2,4-dimethylhexadiene-2,4 and 2,4-dimethylheptadiene-2,4 with 1 mole of peroxide to 1 mole of hydrocarbon, unsaturated monoxides and unsaturated glycol monoacetates were obtained.

3. The experimental data above lead to the conclusion that the oxidation of 1,3-diene hydrocarbons with unsymmetrical structure by acetyl peroxide occurs in two phases by two parallel courses:

a) in one course – in the first phase the oxidation of one double bond occurs with the formation of a monoxide; in the second phase, the oxidation of the monoxide leads to the formation of a dioxide.

b) in the other course – in the first phase the elements of hydrogen peroxide are added in the 1,4-position with the formation of an unsaturated 1,4-glycol monoacetate; in the second phase the oxidation of the glycol monoacetate leads to the formation of an oxidodiol monoacetate.

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* T. p. = C. B. Translation pagination.

5. The experimental data given above are [illegible] with unsymmetrical structures by acetylation of [illegible]

a) In one course — in the first phase the acetylation [illegible] molecule; in the second phase, [illegible]

b) In the other course — in the first phase the [illegible] tion with the formation of [illegible] glycol monoacetate leads to the formation of [illegible]

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* T. p. = C. B. Translation pagination.

REACTIONS OF ACETYLENIC γ-GLYCOLS

IV. ISOMERIZATION OF UNSYMM. METHYL-DI-p-TOLYLBUTINDIOL (1,1-DI-p-TOLYLPENTIN-2-DIOL-1,4)

E. D. Venus-Danilova and Z. V. Printseva

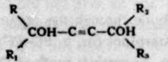
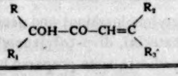
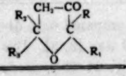
In previous reports [1, 2] isomeric conversions were described for two ditertiary γ-glycols of the acetylene series – unsymm. dimethyl-diphenylbutindiol and unsymm. dimethyl-di-p-tolylbutindiol – in an acidic medium with the formation of ethylenic α-keto alcohols and substituted tetrahydrofuranones-3, as well as the cyclization of these unsaturated α-keto alcohols into the corresponding tetrahydrofuranones-3.

Analogous conversions of secondary-tertiary acetylenic γ-glycols are not described in the literature and therefore the conversions of these acetylenic glycols were carried out under the same conditions.

We synthesized a hitherto unknown unsymm. methyl-di-p-tolylbutindiol (1,1-di-p-tolylpentin-2-diol-1,4) and treated it with alcoholic sulfuric acid solutions of varying concentrations in the cold and with heating.

It turned out that unsymm. methyl-di-p-tolylbutindiol (I) was completely converted into an ethylenic α-keto alcohol – 5,5-di-p-tolylpenten-4-ol-2-one-3 (II) – even with 4% alcoholic acid solution at room temperature, while when heated with 10% acid it gave a cyclic ketone – 2 methyl-5,5-di-p-tolyltetrahydrofuranone-3 (III). This same ketone is also formed by cyclization of 5,5-di-p-tolylpenten-4-ol-2-one-3 in 10% alcoholic sulfuric acid solution.

Isomerization Conditions of γ-Acetylenic Glycols into Ethylenic α-Keto Alcohols and into Tetrahydrofuranones-3.

 $(R)(R_1)COH-C\equiv C-COH(R_2)(R_3)$	 $(R)(R_1)COH-CO-CH=C(R_2)(R_3)$	
1) $R=R_1=CH_3$ $R_2=R_3=C_6H_5$	95% H_2SO_4 alcohol soln., heated at 60-70° for 8 hrs. 93% yield.*	20% H_2SO_4 alcohol soln., heated at 65-70° for 5 hrs. 92% yield.
2) $R=R_1=CH_3$ $R_2=R_3=C_6H_4-CH_3p$	7.5% H_2SO_4 alcohol soln., heated at 30-35° for 6 hrs. 48% keto alcohol and 30% tetrahydrofuranone yield.	18% H_2SO_4 alcohol soln., heated at 60-70° for 7.5 hrs. 84% yield.
3) $R=H$; $R_1=CH_3$ $R_2=R_3=C_6H_4-CH_3p$	4% H_2SO_4 alcohol soln. at room temp. for 6 hrs. 80% yield.	10% H_2SO_4 alcohol soln., heated at 50-55° for 8 hrs. Yield of 60% and resin.

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* 2-Methyl-5,5-diphenylpenten-4-ol-2-one-3 was first considered as a saturated diketone [3].

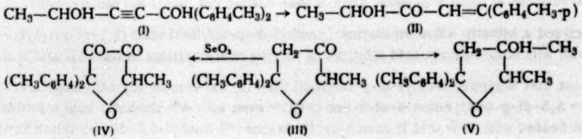
It has been noted earlier [2] that the isomerization of unsymm. dimethyl-di-p-tolylbutindiol into β-ketotetrahydrofuran proceeds with considerably more ease than the isomerization of unsymm. dimethyldiphenylbutindiol. This conversion with unsymm. methyl-di-p-tolylbutindiol occurred under even milder conditions. It can be seen from the table that the substitution of a phenyl radical by a tolyl, as well as one methyl by hydrogen, in the glycol and keto alcohol is conducive to isomerization of the glycol into a keto alcohol and the cyclization of the latter into a tetrahydrofuran.

A reaction product was obtained from the ethylenic α-keto alcohol, 5,5-di-p-tolylpenten-4-ol-2-one-3 (II), with 2,4-dinitrophenylhydrazine. The keto alcohol structure was proved by the formation of di-p-tolylketone and acetaldehyde on ozonization.

2-Methyl-5,5-di-p-tolyltetrahydrofuranone-3 (III) was characterized as the 2,4-dinitrophenylhydrazone, by selenium dioxide oxidation [4, 5] to the cyclic diketone – 2-methyl-5,5-di-p-tolyl-tetrahydrofurandione-3,4 (IV) – as well as by the formation of the tertiary dihydrofuryl alcohol – 2,3-dimethyl-5,5-di-p-tolyltetrahydrofuranol-3 (V) – on treatment with methylmagnesium iodide.

The relative positions of ketone and methylene groups in the tetrahydrofuranone-3 formed were proved by the known structure of the unsaturated α-keto alcohol, in view of the single possibility of its cyclization into a β-ketotetrahydrofuran in an acidic medium [1, 2, 6].

The formation of an unsaturated α-keto alcohol and a β-ketotetrahydrofuran from unsymm. methyl-di-p-tolylbutindiol indicated that the isomerization mechanism of ditertiary and secondary-tertiary γ-glycols of the acetylene series were identical [1].


$CH_3-CHOH-C\equiv C-COH(C_6H_4CH_3)_2 \rightarrow CH_3-CHOH-CO-CH{=}C(C_6H_4CH_3\text{-}p)$
(I)
(II)
SeO₂
(IV)
(III)
(V)

EXPERIMENTAL

Synthesis of Unsymm. Methyl-Di-p-Tolylbutindiol (I)

The glycol was prepared from di-p-tolylacetylenylcarbinol and acetaldehyde through the organomagnesium compound in the usual way [2, 3]. The starting material, di-p-tolylacetylenylcarbinol (m. p. 86-87°), and the di-p-tolyl ketone (m. p. 94-95°), needed for its synthesis, were prepared by I. A. Favorski's method [7].

The yield of unsymm. methyl-di-p-tolylbutindiol (1,1-di-p-tolyl-pentin-2-diol-1,4) was 44%. The m. p. was 103-104° (from benzine). The glycol dissolved readily in ether and alcohol and less readily in benzine (it is not described in the literature).

Found %: C 81.15, 81.21; H 7.35, 7.20; OH 12.38, 12.30. M 288. $C_{19}H_{20}O_2$. Calculated %: C 81.43; H 7.14; OH 12.14. M 280.

The Action of Alcoholic Sulfuric Acid Solution on Unsymm. Methyl-Di-p-Tolylbutindiol

Experiment 1. 100 ml of 4% alcoholic sulfuric acid solution was added to 10 g of methyl-di-p-tolylbutindiol and the reaction mixture became yellow. Stirring was continued for 6 hours at room temperature, while the glycol dissolved, and the solution became yellow in color. After 12 hours the solution was poured into water, was extracted with ether, and the extracts were washed with dilute aqueous soda solution and dried with sodium sulfate. On distillation of the ether, a quite thick, light yellow liquid was obtained with b. p. 204° (1.5 mm), which reacted with potassium permanganate and a chloroform solution of bromine, gave a positive reaction for hydroxyl and carbonyl groups and did not contain ethoxyl groups. The yield was 4 g (80%).

According to analytical data, the material obtained had the structure 5,5-di-p-tolylpenten-4-ol-2-one-3 (it is not described in the literature).

Found %: C 81.13, 81.30; H 7.24, 7.42; OH 6.01, 6.29. M 282.8. $C_{19}H_{20}O_2$. Calculated %: C 81.43; H 7.14; OH 6.07. M 280.

Treatment of the material with 2,4-dinitrophenylhydrazine under the usual conditions [8], immediately precipitated bright red crystals, which gave the pyrazoline reaction; m. p. 78-79° (from alcohol).

Found %: C 65.13; H 5.74; N 11.92, 12.09. $C_{25}H_{25}O_5N_4$. Calculated %: C 65.07; H 5.42; N 12.14.

On ozonizing 2.42 g of the material (b. p. 204° at 1.5 mm) in 45 ml of chloroform for 1 hour, 25 minutes, 0.556 g of ozone was absorbed (theoretical 0.415 g) and 4.05 g of ozonide was isolated as a yellow oil. After the usual decomposition of the ozonide and separation of the neutral and acid ozonolysis products, among the neutral products volatile in steam, acetaldehyde was found, which gave a red color with Schiff's reagent and a dimedone derivative with m. p. 139°, which did not depress the melting point of a dimedone derivative prepared from acetaldehyde. The acetaldehyde could have been formed by decomposition of lactic acid – one of the products of ozonolysis – by excess hydrogen peroxide [9]. From the neutral products, involatile in steam, 1.11 g of di-p-tolyl ketone (61.6%) was isolated with m. p. 93° (mixed m. p.).

The acid ozonolysis products, extracted with ether after decomposition of organic acid salts, smelled of acetic acid and on standing, a small quantity of crystals were isolated with m. p. 177° (from alcohol), which was not depressed by admixture with authentic p-toluic acid. The aqueous residue, after prolonged ether extraction, gave a small quantity of crystals of oxalic acid with m. p. 102° (mixed m. p. and calcium salt).

The fact that di-p-tolyl ketone, acetaldehyde and p-toluic and oxalic acids were obtained by ozonization, confirms the structure of the material.

Experiment 2. On mixing 6 g of methyl-di-p-tolylbutindiol with 60 ml of 10% alcoholic sulfuric acid solution, the solution immediately turned yellow and on heating for 8 hours at 50-55° it became dark brown. The usual method was used to isolate a dark orange, thick liquid, which did not crystallize on standing.

At 1.5 mm the bulk of the material distilled at 185°; 3.6 g (60%) of a thick, slightly yellow uncrystallizable liquid was collected and 2 g of tar.

The material did not contain hydroxyl groups, reacted very slowly with aqueous potassium permanganate solution and did not give an enol reaction with ferric chloride. The reaction for carbonyl groups was positive. According to analytical data and properties, the material obtained was 2-methyl-5,5-di-p-tolyltetrahydrofuranone-3 (it is not described in the literature).

Found %: C 81.28, 81.37; H 7.31, 7.35. M 271. $C_{19}H_{20}O_2$. Calculated %: C 81.43; H 7.14. M 280.

The dinitrophenylhydrazone was obtained by the usual method. A flocculent, orange precipitate immediately came out. The m. p. was 110° (from alcohol).

Found %: C 65.21, 65.47; H 5.87, 5.52; N 12.50, 12.65. $C_{25}H_{25}O_3N_4$. Calculated %: C 65.07; H 5.42; N 12.14.

Oxidation with selenium dioxide was carried out as described in the literature [4]. A solution of 1.4 g of material (b. p. 185° at 1.5 mm) in 5 ml of dioxane was added dropwise to a boiling mixture of 50 ml of moist dioxane and 1.0 g of selenium, which was stirred vigorously. Mixing and boiling of the mixture was continued for 6 hours. The reaction mixture changed from orange to dark red. Selenium separated out on the walls and formed a crimson deposit. Then the mixture was cooled, the precipitated selenium was filtered off, the dioxane was distilled off, the residue was neutralized with aqueous soda solution and the neutral product was extracted with ether. After evaporation of the ether, a dark yellowish-red, thick liquid remained, which distilled in vacuum at 122-128° (2 mm).

Found %: C 77.84; H 6.50. $C_{19}H_{18}O_3$. Calculated %: C 77.55; H 6.12.

The liquid obtained (0.4 g) was converted into a quinoxaline according to a literature method [10], by heating with o-phenylenediamine (0.15 g) for 15-20 minutes. After recrystallization from alcohol it had m. p. 197°.

Found %: N 7.49. $C_{25}H_{22}ON_2$. Calculated %: N 7.65.

The aqueous solution, after extraction of the neutral selenium dioxide oxidation products, was evaporated to small volume and acidified with dilute sulfuric acid. The solution was extracted with ether and after distillation of the solvent, the residue yielded a silver salt (through the ammonium salt), corresponding to that of methyl-di-p-tolyldiglycolic acid.

Found %: C 41.69; H 3.19; Ag 40.12. $C_{19}H_{18}O_5Ag_2$. Calculated %: C 42.06; H 3.32; Ag 39.89.

The formation of a mixed diglycolic acid occurred as a result of further oxidation of tetrahydrofurandione-3,4 with opening of the five-membered ring between positions 3 and 4. Similar cases are described in the literature [4, 11].

2,3-Dimethyl-5,5-di-p-tolyltetrahydrofuranol-3 was synthesized from 2.4 g of 2-methyl-5,5-di-p-tolyltetrahydrofuranone-3 by treatment with methylmagnesium iodide, prepared from 0.4 g of magnesium and 2.5 g of methyl iodide. After the usual isolation of the synthesis product, 2 g (63%) of a thick, colorless liquid was obtained with b.p. 112-114° (2 mm), which gave reactions for hydroxyl and carbonyl groups.

This material may be considered a tertiary alcohol of the tetrahydrofuran series – 2,3-dimethyl-5,5-di-p-tolyltetrahydrofuranol-3, which is not described in the literature.

Found %: C 80.83, 81.00; H 8.36, 8.38; OH 6.01. M 288. $C_{20}H_{24}O_2$. Calculated %: C 81.08; H 8.11; OH 5.74. M 296.

The Action of Alcoholic Sulfuric Acid Solution on 5,5-Di-p-Tolylpenten-4-ol-2-one-3

1.5 g of 5,5-di-p-tolylpenten-4-ol-2-one-3 (b. p. 204° at 1.5 mm) was heated at 50-55° for 8 hours with 20 ml of 10% alcoholic sulfuric acid solution under vigorous stirring. After a day, the turbid yellow mixture was poured into water, extracted with ether, washed with aqueous soda solution and dried over sodium sulfate. After evaporation of the ether the material obtained distilled at 186° (2 mm). In its properties and its 2,4-dinitrophenylhydrazone (m. p. 110°, mixed m. p.), the material corresponded to a ketone of the tetrahydrofurane series – 2-methyl-5,5-di-p-tolyltetrahydrofuranone-3. The yield was about 70%.

SUMMARY

1. The secondary-tertiary γ-glycol of the acetylene series, 1,1-di-p-tolylpentin-2-diol-1,4 was synthesized and its conversion in an alcohol solution with a sulfuric acid catalyst was studied.

2. It was found that the glycol was isomerized by a 4% acid alcohol solution at normal temperature into the ethylenic α-keto alcohol – 5,5-di-p-tolylpenten-4-ol-2-one-3, and by heating with 10% sulfuric acid solution it was converted into a tetrahydrofuryl ketone – 2-methyl-5,5-di-p-tolyltetrahydrofuranone-3.

3. It was shown that 5,5-di-p-tolylpenten-4-ol-2-one-3 was cyclized in 10% sulfuric acid alcohol solution into 2-methyl-5,5-di-p-tolyltetrahydrofuranone-3.

4. The tetrahydrofurane diketone – 2-methyl-5,5-di-p-tolyltetrahydrofurandione-3,4 and the tetrahydrofuryl alcohol – 2,3-dimethyl-5,5-di-p-tolyltetrahydrofuranol-3, were synthesized from 2-methyl-5,5-di-p-tolyltetrahydrofuranone-3.

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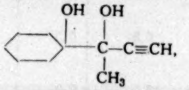
TERTIARY TRIOLS OF THE ACETYLENE SERIES AND THEIR REACTIONS

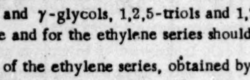
X. POTASSIUM PERMANGANATE OXIDATION OF THE ETHYLENIC TRIOLS: 2,3,6-TRIMETHYLHEPTEN-4-TRIOL-2,3,6; 3,4,7-TRIMETHYLOCTEN-5-TRIOL-3,4,7; 2,5-DIMETHYL-5-(1-HYDROXYCYCLOHEXYL)-PENTEN-3-DIOL-2,5 AND 2,4-DI-(1-HYDROXYCYCLOHEXYL)-BUTEN-3-OL-2.

V. I. Nikitin and I. M. Timofeeva

It was shown earlier [1] that the action of aqueous potassium permanganate solution on tertiary acetylenic triols, besides forming products indicating an oxidation reaction breaking the triple bond, always forms oxalic acid, indicating that some other reaction also occurs.

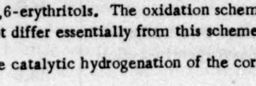
V. N. Krestinsky had to assume that there were two tautomeric forms of tetramethylbutindiol – acetylene and diene – to explain the formation of oxalic acid by oxidation of the former with potassium permanganate [2]. However, this explanation could not be adopted for this case as oxalic acid was also produced by oxidation of 2-(1-hydroxycyclohexyl)-butin-3-ol-2  which cannot be explained by any tautomeric effect. Therefore, an oxidation scheme of hydroxyl-containing acetylene derivatives was given in the above work by one of us, which develops further the classical oxidation scheme for double bonds of olefins, worked out by E. E. Vagner [3]. According to this scheme the acetylene bond in hydroxyl-containing acetylene derivatives is oxidized by potassium permanganate in such a way that the addition of hydrogen peroxide elements by the triple bond occurs during the first phase of the reaction. An unsaturated glycol is formed which is further oxidized, adding further hydrogen peroxide elements at the double bond and then converting into the diketone. The oxidizing agent reacts further with the diketone formed (diketotriol) by simultaneously attacking the bond between the carbons which have carbonyl oxygen atoms, i.e., at the position of the former triple bond, as well as the bond between the carbons, one of which has a carbonyl oxygen and the other a hydroxyl, i.e., at the end of the former triple bond, which results in the formation of oxalic acid. This scheme also occurs during the oxidation of acetylenic α-alcohols, α-, β- and γ-glycols, 1,2,5-triols and 1,2,5,6-erythritols. The oxidation scheme for all the derivatives listed above and for the ethylene series should not differ essentially from this scheme.

Four glycerins of the ethylene series, obtained by the catalytic hydrogenation of the corresponding acetylenic glycerins [4] were oxidized in the present work.



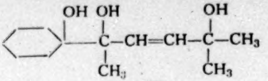
$$CH_3-\overset{OH}{\underset{CH_3}{C}}-\overset{OH}{\underset{CH_3}{C}}-CH=CH-\overset{OH}{\underset{CH_3}{C}}-CH_3$$

(I)

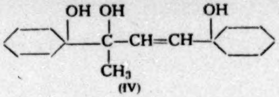


$$C_2H_5-\overset{OH}{\underset{CH_3}{C}}-\overset{OH}{\underset{CH_3}{C}}-CH=CH-\overset{OH}{\underset{CH_3}{C}}-CH_3$$

(II)



(III)



(IV)

Acetone and acetic, formic, α-hydroxyisobutyric and oxalic acids were formed by oxidation of 2,3,6-trimethylhepten-4-triol-2,3,6 (I). Acetone, methyl ethyl ketone, acetic acid, traces of formic, α-hydroxyisobutyric and oxalic acids were formed by oxidation of 3,4,7-trimethylocten-5-triol-3,4,7 (II). 2,5-Dimethyl-5-(1-hydroxycyclohexyl)-penten-3-diol-2,5 (III) gave on oxidation acetone, acetylcyclohexanol and acetic, α-hydroxyisobutyric and oxalic acids, while 2,4-di-(1-hydroxycyclohexyl)-buten-3-ol-2 gave cyclohexanone and acetic, α-hydroxyhexahydrobenzoic, adipic and oxalic acids.

Thus, the same products were obtained by oxidizing ethylenic glycerins as those obtained from the corresponding acetylenic glycerins [1].

A special feature of ethylenic triol oxidations is the fact that they give a relatively larger amount of oxalic acid than with triols of the acetylene series. However, the reverse occurs in the formation of α-hydroxyisobutyric acid (Table 1).

TABLE 1

Quantitative Data on the Formation of α-Hydroxyisobutyric and Oxalic Acids by Oxidation of Tertiary Acetylenic and Ethylenic Triols.

Material	Name of oxidized material	Amount of oxidized material (in g)	α-Hydroxyisobutyric acid obtained		Oxalic acid obtained	
			(in g.)	in moles (1 M oxidized material)	(in g.)	in moles (1 M oxidized material)
(I)	2,3,6-Trimethylhepten-4-triol-2,3,6	6.5	0.1	0.03	1.3	0.42
(II)	3,4,7-Trimethylocten-5-triol-3,4,7	10.5	2.0	0.37	1.8	0.38
(III)	2,5-Dimethyl-5-(1-hydroxycyclohexyl)-penten-3-diol-2,5	8.3	2.0	0.53	1.8	0.54
(IV)	2,4-Di-(1-hydroxycyclohexyl)-buten-3-ol-2	5.0	1.0*	0.4*	0.85	0.5
(I')	2,3,6-Trimethylheptin-4-triol-2,3,6	16.49	4.7	0.5	0.6	0.074
(II')	3,4,7-Trimethyloctin-5-triol-3,4,7	13.9	4.1	0.57	0.95	0.15
(III')	2,5-Dimethyl-5-(1-hydroxycyclohexyl)-pentin-3-diol-2,5	16.9	4.2	0.54	3.2	0.4
(IV')	2,4-Di-(1-hydroxycyclohexyl)-butin-3-ol-2	17.4	4.6	0.47*	1.6	0.21

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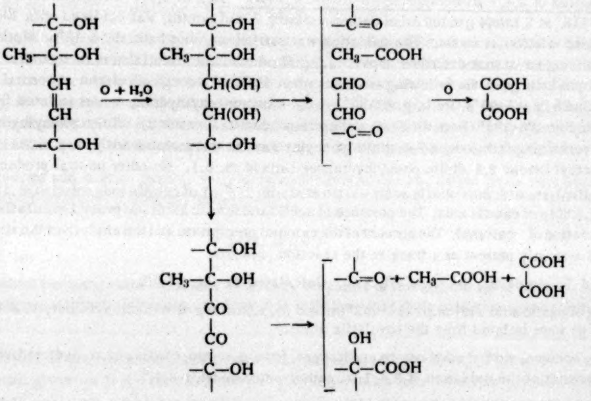
* α-Hydroxyhexahydrobenzoic acid.

We consider that these facts are due to some special features which occur in addition to the basic similarity in the oxidation mechanism of ethylenic and acetylenic glycerins. As a matter of fact the triple bond in acetylenic glycerins oxidizes with the formation of an unsaturated glycol which immediately converts into the diketone and it is the latter which oxidizes further into the end product. The oxidation of the double bond of ethylenic glycerins in the first phase results in the formation of a disecondary glycol which, in the following phase of the oxidation is apparently capable of oxidizing further not only through the diketone but also in other directions, in particular, at bonds between carbons with tertiary and secondary hydroxy groups (i.e., at the ends of the former double bond) into a glycol aldehyde which is followed by further oxidation into oxalic acid by the following scheme:



EXPERIMENTAL

Oxidation of 2,3,6-trimethylhepten-4-triol-2,3,6 (I). 760 ml of 3% potassium permanganate solution (5 active oxygen atoms to 1 molecule of oxidizable material) was slowly added dropwise to a mechanically stirred mixture of 8 g of 2,3,6-trimethylhepten-4-triol-2,3,6 (I) (m. p. 116-117° [4]), 75 ml of water and 1 g of potash. The oxidation was carried out at room temperature. When all the potassium permanganate solution had been introduced, the precipitated manganese dioxide was filtered off and washed with water and the washing water and filtrate were combined. A distillate (about 650 ml) containing the neutral products was obtained from the filtrate. The residual salt solution was extracted with ether until the involatile neutral products were completely extracted. After drying the ether extract and distilling off the ether, 1.5 g of material remained with m. p. 116-117°, which was the original triol. The distillate with the neutral products was salted out with sodium sulfate and concentrated by several distillations. Each time the volume of distillate taken off was equal to half the original volume. The final distillate was 200 ml. The low boiling products were distilled from this volume with a fractionating column of 27 theoretical plates. A fraction was taken off at normal pressure with b. p. 53-57°, which gave a 2,4-dinitrophenylhydrazone with m. p. 123° (from ethyl alcohol); a mixed m. p. with authentic acetone 2,4-dinitrophenylhydrazone was not depressed. No other neutral products were isolated.

The solution of acid salts, remaining after extraction of the neutral products, was acidified with sulfuric acid and the volatile acids were distilled in steam. The distillate with the volatile acids was titrated with 114.07 ml of caustic soda solution (0.1075 N) which corresponded to 0.4895 g of caustic soda. The presence of acetic and formic acids was proved qualitatively by a cacodyl test and by the formation of a calomel. The amount of calomel precipitate showed that there was a significant amount of formic acid in the reaction products. This was also confirmed by analysis of the silver salt.

Found %: Ag 67.00, 67.10. $C_2H_3O_2Ag$. Calculated %: Ag 64.07.

The involatile acids were neutralized with caustic soda. Then oxalic acid was precipitated as the calcium salt with a saturated solution of calcium chloride and 1.3 g of oxalic acid was obtained from this with m. p. 101-102°; its mixed m.p. with authentic oxalic acid was not depressed. The filtrate, separated from the calcium oxalate, was acidified with hydrochloric acid and extracted with ether for 24-30 hours in an extractor. After the ether was distilled off, 0.1 g of a crystalline acid with m. p. 79° (from benzene) remained. This did not depress the melting point of authentic α-hydroxyisobutyric acid.

Thus, acetone and acetic, formic, oxalic and α-hydroxyisobutyric acids were isolated from the oxidation of 2,3,6-trimethylhepten-4-triol-2,3,6.

Oxidation of 3,4,7-trimethylocten-5-triol-3,4,7 (II). 12 g of 3,4,7-trimethylocten-5-triol-3,4,7 (II) (b. p. 117-118° at 2 mm[4]) in 100 ml of water containing 2 g of potash, was oxidized with 1041 ml of 3% potassium permanganate solution as above. The oxidation was carried out on a bath at 14-15°. Working up of the products was analogous to that described above. 1.5 g of unoxidized material was recovered. The distillate with the neutral products gave the following fractions when distilled through a column at normal pressure; 1st b. p. up to 65°; 2nd b. p. 65-71°; 3rd b. p. 71-85°. A 2,4-dinitrophenylhydrazone was isolated from the 1st fraction, which melted at 125-126° (from alcohol) and corresponded to acetone 2,4-dinitrophenylhydrazone. From each of the two remaining fractions, a 2,4-dinitrophenylhydrazone was isolated with m. p. 112-113°, which corresponded to methyl ethyl ketone 2,4-dinitrophenylhydrazone (mixed m. p.). No other neutral products were isolated.

The distillate with the volatile acids was titrated with 288 ml of caustic soda solution (0.1157 N), which corresponded to 1.3338 g of caustic soda. The presence of acetic and formic acids was proved qualitatively by a cacodyl test and the formation of calomel. The amount of the calomel precipitate and the analysis of the silver salt showed that formic acid was only present as a trace in the reaction products.

Found %: Ag 64.90, 64.82. $C_2H_3O_2Ag$. Calculated %: Ag 64.07.

1.8 g of oxalic acid with m.p. 101-102° (mixed m.p.) and 2 g of α-hydroxyisobutyric acid with m.p. 79° (mixed m. p) were isolated from the involatile acids.

Thus, acetone, methyl ethyl ketone and traces of formic, acetic, oxalic and α-hydroxyisobutyric acids were obtained as a result of the oxidation of 3,4,7-trimethyl-octen-5-triol-3,4,7.

Oxidation of 2,5-dimethyl-5-(1-hydroxycyclohexyl)-penten-3-diol-2,5 (III). 10 g of 2,5-dimethyl-5-(1-hydroxycyclohexyl)-penten-3-diol-2,5 (III) (m. p. 102-103° [4]) in 100 ml of water, containing 1 g of potash, was oxidized with 780 ml of 3% potassium permanganate solution as described above. The oxidation was carried out at 16°.

The isolation and examination of the oxidation products was also carried out as in the previous cases. 1.7 g of unreacted starting material was isolated. The following fractions were isolated from the distillate containing the neutral products: 1st b. p. 55-56° and 2nd b. p. 150-200°.

Acetone, 2,4-dinitrophenylhydrazone with m. p. 123° (mixed m. p.) was obtained from the 1st fraction. A semicarbazone was isolated from the 2nd fraction, which melted at 194-195° and corresponded to acetylcyclohexanol semicarbazone and this was confirmed by a mixed m. p. No other neutral products were isolated.

The volatile acids were neutralized by titration with 132.5 ml of caustic soda solution (0.0938 N), which corresponded to 0.4968 g of caustic soda. Acetic acid was found in the distillate with the volatile acids by the cacodyl test, though no formic acid was found.

Found %: Ag 62.50, 62.00. $C_2H_3O_2Ag$. Calculated %: Ag 64.07.

By methods analogous to those described above, 1.8 g of oxalic acid with m. p. 101-102° and 2 g of α-hydroxyisobutyric acid with m. p. 79° (mixed m. p.) were isolated from the involatile acids.

In this way, acetone, acetylcyclohexanol and acetic, oxalic and α-hydroxyisobutyric acids were obtained from the oxidation of 2,5-dimethyl-5-(1-hydroxycyclohexyl)-penten-3-diol-2,5.

Oxidation of 2,4-di-(1-hydroxycyclohexyl)-buten-3-ol-2 (IV). 8 g of 2,4-di-(1-hydroxycyclohexyl)-buten-3-ol-2 (IV) (m. p. 111-112° [4]) in 75 ml of water containing 1 g of potash was oxidized with 550 ml of 3% potassium permanganate solution. The oxidation was carried out at room temperature and proceeded extremely slowly. The permanganate solution was introduced over 10 days with continuous mechanical stirring. The reaction products were treated as in the previous experiments. 3.0 g of unoxidized alcohol was recovered.

A fraction, boiling over the range 100-150° at normal pressure, was isolated from the distillate with the neutral products. This fraction yielded a semicarbazone with m. p. 164-165° (from methyl alcohol), which corresponded to cyclohexanone semicarbazone (mixed m. p.). No other neutral products were isolated. Titration of the volatile acids required 67.6 ml of caustic soda solution (0.0035 N), which corresponded to 0.2535 g of caustic soda. The presence of acetic acid was proved qualitatively by a cacodyl test. Formic acid was not found. A silver salt was prepared.

Found %: Ag 63.00, 63.00. $C_2H_3O_2Ag$. Calculated %: Ag 64.07.

1.7 g of oxalic acid with m. p. 101-102° (mixed m. p.), was obtained from the involatile acids. After separation of the calcium oxalate, the salt solution was acidified with hydrochloric acid and extracted with ether for 20-25 hours in an extractor. After distillation of the ether from the extract, crystals were left, from which hot benzene extracted 1 g of α-hydroxyhexahydrobenzoic acid with m. p. 105-106°. The residue (0.95 g), which did not dissolve in benzene, melted at 152-153° and was found to be adipic acid. Both α-hydroxyhexahydrobenzoic and adipic acids were identified by mixed m. p.s with corresponding samples of the authentic acids.

Thus, cyclohexanone and acetic, oxalic, α-hydroxyhexahydrobenzoic and adipic acids were obtained from the oxidation of 2,4-di-(1-hydroxycyclohexyl)-buten-3-ol-2.

SUMMARY

1. In the potassium permanganate oxidation of tertiary ethylenic glycerins, the same products were formed as from the corresponding acetylenic glycerins and from this it follows that their oxidation mechanism is principally the same.

2. A special feature of the oxidation mechanism of tertiary ethylenic glycerins, in comparison with the corresponding acetylenic glycerins is the fact that the acetylenic glycerins form ethylenic glycols at the triple bond in the first phase of oxidation, and these immediately oxidize into diketones with subsequent oxidative cleavage of the latter into the end products.

The corresponding ethylenic glycerins form disecondary glycols at the double bond in the first phase of oxidation, and these glycols are capable not only of oxidizing into diketones, but also,like diketones directly undergo oxidative cleavage which only shows up in the end products in the quantity ratio.

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* T. p. = C. B. Translation pagination.

slowly. The permanganate solution was decolorized after 12 hours [illegible]. The washing products were treated as in the previous experiments. 5.2 g of unsaturated acids was recovered.

[illegible] products. This fraction yielded a [illegible] corresponded in [illegible] of the potassium salt required [illegible] acids. The presence of [illegible] A silver salt was prepared.

Found %: [illegible]

[illegible]

The cyclohexanone and acetic [illegible]

SUMMARY

1. In the potassium permanganate oxidation of tertiary [illegible] the corresponding [illegible]

2. [illegible]

The corresponding [illegible]

LITERATURE CITED

[1] V. I. Nikitin and [illegible], J. Gen. Chem. 25, [illegible] (1955) (T. p. [illegible]).*

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BORON FLUORIDE AS A CATALYST IN ORGANIC CHEMISTRY

XII. ALKYLATION OF BENZENE BY PSEUDOBUTYLENE USING A $BF_3 \cdot H_3PO_4$ CATALYST

S. V. Zavgorodny, L. S. Shvetsova and B. S. Khromykh

The alkylation of aromatic hydrocarbons by olefins is usually carried out in the presence of the following catalysts: aluminosilicates, H_2SO_4, H_3PO_4, HF, $AlCl_3$ and BF_3. Benzene alkylation by propylene in the presence of sulfuric acid was studied in detail by Yu. G. Mamedaliev [1], and with phosphoric acid and aluminosilicate catalysts by Yu. L. Khmelnitsky, A. I. Doladygin, A. I. Skoblo and A. V. Guseva [2, 3], while A. V. Topchiev and Ya. M. Paushkin [4-6] studied the reaction in the presence of molecular compounds of boron trifluoride with different organic and inorganic materials.

The alkylation of benzene with pseudobutylene, isolated from by-products of divinyl production by S. V. Lebedev's method, was studied in this report. A molecular compound of boron fluoride and orthophosphoric acid was used as the catalyst and was extremely effective for this reaction. The reaction mixture heated up to 60-80° 20-30 minutes after the introduction of pseudobutylene. The molecular ratio of reagents and catalyst as well as the temperature substantially affected the yield and composition of the alkylate. Molecular ratios for benzene, pseudobutylene and catalyst of from 4.5 : 1 : 0.4 to 3.5 : 1 : 0.3 at 30° were the optimal reaction conditions when an 83% yield of alkylate was obtained, containing 83-87% of sec.-butylbenzene. A decrease in catalyst to 0.1 mole per 1 mole of pseudobutylene (keeping the same reagent ratio and temperature) lowered the alkylate yield to 67%, while the proportion of sec.-butylbenzene in the alkylate hardly changed.

An important property of $BF_3 \cdot H_3PO_4$ catalyst is that it does not mix with either the reagents or the alkylation products and when the reaction mixture settles, it is easily separated in the lower layer and can be used again in several experiments. Alkylation in the presence of a previously used catalyst, with a ratio of benzene, pseudobutylene and catalyst of 1 : 1 : 0.3 and a reaction temperature of 50-60°, does not differ essentially from the reaction carried out with freshly prepared catalyst (in intensity of pseudobutylene absorption, heating of reaction mixture and alkylate yield). On re-using the same catalyst, its activity gradually decreases in the third and fourth experiments. The decrease in catalyst activity after repeated use is probably due to boron trifluoride losses by mechanical removal with unabsorbed pseudobutylene and, partially, by separation with alkylate. Therefore, if a small additional amount of boron trifluoride is added to a catalyst that has been used in a series of experiments, its activity is restored. A temperature in the range 30-60° does not usually have any particular effect on the reaction.

As numberous experiments have shown, the compound $BF_3 \cdot H_3PO_4$ may be considered as a monoalkylation catalyst. Although we varied the molar ratios of reagents and catalyst and the temperature, within the range 20-80°, an alkylate with 41% of di-sec.-butylbenzene was obtained only with a ratio of benzene, pseudobutylene and $BF_3 \cdot H_3PO_4$ of 0.6 : 1 : 0.1. Usually, however, the proportion of di-sec.-butylbenzene was 10-24%. The latter was mainly the para-derivative.

The experimental data are given in the table.

EXPERIMENTAL

Pseudobutylene needed for carrying out the reaction was isolated from a pseudobutylene-divinyl fraction containing 70-80% pseudobutylene by polymerizing the divinyl with metallic sodium.

Alkylation of Benzene by Pseudobutylene Using a $BF_3 \cdot H_3PO_4$ Catalyst

Expt. No.	Amount taken for reaction (g)			Molar ratios of reagents and catalyst	Reaction conditions		Alkylate obtained							Recovered benzene (g)
	Benzene	Pseudobutylene	$BF_3 \cdot H_3PO_4$		Temperature	Time for pseudobutylene addition, (hr)	Total		Fraction No	Yield (% theoretical	Boiling point	d_4^{20}	n_D^{20}	
							g	%						
1	114.9	17.8	22.4	4.5 : 1 : 0.4	to 30°	3	35.5	83.4	1	14.5	169—170°	0.8565	1.4891	85.5
									2	58.6	171—173	0.8620	1.4890	
2	114.8	24.3	16.4	3.5 : 1 : 0.3	to 30	1¹/₆	48.1	82.5	1	7.5	165—170	0.8620	1.4886	76.3
									2	60.9	171—173	0.8640	1.4390	
3	16.0	7.0	13.0	1.7 : 1 : 0.6	to 45	2¹/₂	14.0	83.6	1	59.8	170—200	0.8680	1.4885	2.0
									2	11.9	230—245	0.8700	1.4890	
4	98.2	23.8	17.1	3 : 1 : 0.3	to 30	2¹/₂	45.2	79.3	1	11.4	168—170	0.8624	1.4910	63.7
									2	49.6	171—174	0.8594	1.4910	
									3	13.0	175—200	0.8555	1.4900	
5	79.0	18.7	15.0	3 : 1 : 0.3	to 65	1¹/₂	34.3	76.7	1	68.5	170—200	0.8670	1.4900	48.0
6	27.3	20.8	17.4	1 : 1 : 0.3	50—60	1¹/₆	38.0	78.9	1	2.9	120—169	0.8546	1.4905	2.6
									2	56.5	170—175	0.8602	1.4889	
									3	16.2	92—94 (4 mm)	0.8592	1.4878	
7	27.0	20.6	From a previous experiment	1 : 1 : 0.3	50—60	1¹/₃	36.6	76.8	1	6.0	120—169	0.8592	1.4858	6.4
									2	50.9	170—175	0.8583	1.4880	
									3	16.3	96—99 (5 mm)	0.8588	1.4865	
8	73.2	49.5	27.0	1 : 1 : 0.2	to 50	3¹/₂	88.5	74.1	1	8.5	120—170		1.4844	23.8
									2	53.9	171—175	0.8616	1.4890	
									3	10.9	99—103 (5 mm)	0.8592	1.4870	
									4	0.6	115—120 (5 mm)	0.8569	1.4865	

(continued)

Expt. No.	Amount taken for reaction (g)			Molar ratios of reagents and catalyst	Reaction conditions		Alkylate obtained							Recovered benzene (g)
	Benzene	Pseudo-butylene	$BF_3 \cdot H_3PO_4$		Temperature	Time for pseudo-butylene addition, (hr)	Total g	Total %	Fraction No.	Yield (% theoretical)	Boiling point	d_4^{20}	n_D^{20}	
9	26.1	17.4	15.1	1 : 1 : 0.3	to 60	$1^1/_2$	29.3	70.1	1 2	62.1 5.7	170—200° 230—245	0.8660 0.8670	1.4910 1.4915	6.8
10	26.4	18.1	From a previous experiment	1 : 1 : 0.3	to 55	$1^2/_3$	32.7	74.1	1 2	63.7 10.0	170—200 230—245	0.8680 0.8600	1.4895 1.4985	4.6
11	26.7	17.0	From a previous experiment	1 : 1 : 0.3	to 30	$5^1/_2$	21.4	52.6	1 2	41.6 6.4	170—200 230—245	0.8640 0.8620	1.4920 1.4930	3.4
12	25.7	17.4	From a previous experiment	1 : 1 : 0.3	to 50	$2^1/_6$	28.3	67.6	1 2	54.3 8.8	170—200 230—245	0.8660 0.8630	1.4890 1.4875	6.2
13	26.3	19.0	16.0	1 : 1 : 0.3	75—80	$1^1/_3$	27.0	59.7	1 2	47.4 6.8	170—200 230—245	0.8690 0.8610	1.4892 1.4870	10.6
14	26.9	19.6	From a previous experiment	1 : 1 : 0.3	75—80	$1^1/_4$	24.7	53.0	1 2	44.5 6.3	170—200 230—245	0.8710 0.8830	1.4890 1.4889	11.0
15	47.9	25.7	7.3	1.3 : 1 : 0.1	to 60	2	41.2	67.1	1 2 3	7.5 52.9 6.7	120—169 170—175 92—95 (5mm)	— — —	1.4854 1.4880 1.4850	20.5
16	39.1	47.1	14.1	0.6 : 1 : 0.1	to 55	4	70.8	82.2	1 2 3 4 5	2.1 42.4 27.2 6.6 2.3	120—170 171—176 98—102 (5mm) 110—113 (7mm) 120—135 (7mm)	— 0.8570 — — —	1.4780 1.4860 1.4860 1.4860 1.4853	8.6
17	27.1	56.1	14.6	0.35 : 1 : 0.1	to 65	10	36.8	44.2	1 2	31.2 10.0	170—200 230—245	0.8650 0.8600	1.4848 1.4860	3.3

Footnote. In Experiment 12, a further 1.95 g of BF_3 was added to the catalyst, separated from the reaction products of Experiment 11.

The catalyst $BF_3 \cdot H_3PO_4$ was prepared by saturating anhydrous orthophosphoric acid with boron trifluoride until the weight absorbed corresponded to equal molecular proportions of boron trifluoride and the acid.

The anhydrous orthophosphoric acid was stirred and saturated with boron trifluoride in a round-bottomed three-necked flask of 250 ml capacity and fitted with a mechanical stirrer with a mercury seal, a reflux condenser and a gas inlet. Benzene was added to the catalyst obtained in this way and pseudobutylene was introduced into the mixture at 1.5-6 liters/hour at room temperature and with vigorous stirring. Usually, at the beginning, the absorption of pseudobutylene proceeded comparatively slowly, but 20-30 minutes from the beginning of the reaction it sharply increased, and the alkylation was accompanied by a heating effect. The reaction mixture was heated to 80° in various experiments. After the introduction of a definite amount of pseudobutylene, the mixture was stirred for a further 1.5-3 hours. The reaction mixture was transferred to a separating funnel, the catalyst was separated off for further use and the alkylate was washed with water, 5% soda solution and again with water, dried with calcium chloride and distilled. The unreacted benzene was distilled off at atmospheric pressure and then the alkylation products were fractionated and they distilled almost completely. The residue in the flask usually amounted to 0.2-3 g in 15-50 g of alkylate taken for fractionation, and was a brown oil. In one of the experiments this oil had d_4^{18} 0.8701, n_D^{18} 1.4880.

To identify the alkylation products, all the fractions with similar boiling point, specific gravity and refractive index were combined and distilled a second time through a fractionating column. Two products were isolated: sec-butylbenzene and p-di-sec-butylbenzene.

Sec.-butylbenzene. The proportion of this in the alkylate was 71-90%.

B. p. 171-173°, d_4^{20} 0.8620, n_D^{20} 1.4890, MR_D 44.93; Calc. 44.78. Literature data: [7]: b. p. 173.3°, d_4^{20} 0.8622, n_D^{20} 1.4920

p-Sec.-butylacetanilide was obtained by nitrating the sec.-butylbenzene, reducing the nitroderivative to the amine and acetylating the latter, and had m. p. 125-126° [8].

p-Di-sec.-butylbenzene. The proportion of this in the alkylate was 10-40% (depending on conditions).

B. p. 104-107° (5-6 mm), d_4^{20} 0.8583, n_D^{20} 1.4872, MR 63.75; Calc. 63.25. Literature data [7]: b. p. 240°, d_4^{20} 0.8573, n_D^{20} 1.4878.

Oxidation of p-di-sec.-butylbenzene with 30% nitric acid yielded terephthalic acid, which was identified by esterification with methanol to dimethyl terephthalate with m.p. 139-140°. Bromination of p-di-sec-butylbenzene in carbon tetrachloride gave a monobromide; the latter was oxidized with 30% nitric acid to bromoterephthalic acid with m. p. 180-182°

SUMMARY

The alkylation of benzene by pseudobutylene using a $BF_3 \cdot H_3PO_4$ catalyst, was investigated with various molecular proportions of the reagents and the catalyst and at temperatures of 30-80°. It was shown that the molecular compound $BF_3 \cdot H_3PO_4$ was an extremely effective catalyst for the alkylation of benzene by pseudobutylene. The catalyst did not mix with the reagents and the alkylate, was easily separated as the lower layer, and could be used many times over.

The most favorable conditions for obtaining mono-sec.-butylbenzene gave a yield of 73%, when the molar proportions of benzene, pseudobutylene and catalyst were 4.5 : 1 : 0.4.

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CATALYTIC REACTIONS WITH METALLIC ALUMINUM

I. ALKYLATION OF BENZENE WITH ALKYL BROMIDES

M. B. Turova-Polyak and M. A. Maslova

A series of papers [1-5] on benzene alkylation with aliphatic halides in the presence of activated and inactive metallic aluminum, showed that it was possible to obtain benzene homologs in satisfactory yields. V. D. Azatyan [1], N. G. Sidorova, I. P. Tsukervanik and Z. Kh. Abidova [6] mention in their papers the formation of a "dark red liquid" or "an oily lower layer" during alkylation, which was apparently, a complex compound often formed in the reaction of aluminum halide salts with aromatic hydrocarbons and halogen derivatives. The catalytic properties of this compound, were not, however, examined in these papers.

As we considered that the complex formed would possess reasonably high catalytic properties, we investigated the alkylation of benzene with ethyl, n-propyl and n-butyl bromide and showed that this complex compound could be used repeatedly as catalyst in the reaction. Alkylation of benzene with ethyl bromide was especially effective in the presence of this catalyst. The ethylbenzene yield in some cases was greater than the yield obtained by using metallic aluminum. With prolonged use the yield of ethylbenzene gradually decreased while the polyethylbenzene content increased.

Furthermore, we examined the relation of yield of alkylation products to reaction mixture composition and established that an increase in benzene from 3 : 1 to 6 : 1 in the reaction mixture produced a higher yield of alkylbenzene; a further increase in the amount of benzene in the mixtures did not affect the increase in alkylbenzene yield. We also established that there was an increase in alkylbenzene yield with an increase in the molecular weight of halogen derivative: under optimal conditions the yield of ethylbenzene was 68.5%, propylbenzene 76.5% and butylbenzene 83.7% (on halogen derivative taken). These results contradict the data given by B. N. Dolgov, I. I. Sorokina and A. E. Cherkasov [5] according to which the monoalkylbenzene yield decreased with an increase in the molecular weight of the halogen derivative.

Isopropyl- and isobutylbenzenes were formed by the alkylation of benzene with n-propyl bromide and n-butyl bromide. We explained the formation of isostructural hydrocarbons by the fact that, on the one hand, the olefin was the alkylating agent and, on the other, that aluminum chloride, or the complex compound, formed during the reaction, had an isomerizing effect.

EXPERIMENTAL

The reaction was carried out by Azatyan's method [1]. The starting materials were dried carefully and distilled immediately before the experiments. Also the aluminum turnings were cut on a lathe immediately before the experiments and stored under dry benzene. Materials whose constants agreed with literature data, were used in the reaction. The mixture of benzene, halogen derivative, and aluminum turnings, was heated on a water bath (for the synthesis of ethylbenzene, to 65-72°, for propylbenzene 75-80°, and for butylbenzene 82-85°) for 1.5-2 hours until the reaction began, which was shown by a change in the solution color, the appearance of hydrogen bromide bubbles and a reduction in the reaction mixture temperature by 5-10°; after this, heating was discontinued, but, despite this, the reaction proceeded to develop energetically with copious evolution of hydrogen bromide and was complete in 10-15 minutes. After this the reaction mixture was again heated for 35-40 minutes at 70-80° (until evolution of hydrogen bromide ceased) and stood for 2 hours at room temperature. A red-brown oily layer separated at the bottom of the flask (complex) and the liquid above it became transparent. The upper layer was poured off, decomposed with dilute acid, washed by a suitable method, dried and distilled.

Alkylation of Benzene with Ethyl Bromide

The experiments were carried out using 0.01 g-atom of aluminum. The results are given in Table 1.

TABLE 1

Ratio benzene : ethyl bromide	Yield of alkylation product (%)	Composition of alkylation products (in %)	
		ethylbenzene	polyethylbenzene
3:1	46.0	90.9	9.1
4:1	46.4	93.0	7.0
5:1	53.7	94.7	5.3
6:1	68.4*	95.0	5.0
8:1	67.4	96.0	4.0

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* Without additional heating of the reaction mixture for 35-40 minutes, the yield of alkylation product was reduced to 48.2%.

In a separate series of experiments it was shown that the maximum yield of ethylbenzene was obtained with 0.01 g-atom of aluminum to 1 mole of halogen derivative (Table 2); therefore all subsequent experiments were carried out using 0.01 g-atom of aluminum.

TABLE 2

Ratio benzene : : ethyl bromide	Amount of aluminum (in g-atom)	Yield of alkylation product (in %)	Composition of alkylation products (in %)	
			ethylbenzene	polyethylbenzene
6:1	0.005	47.9	63.0	37.0
6:1	0.01	68.4	90.0	10.0
6:1	0.02	67.4	96.3	3.7

To find out the possibility of using the complex as a catalyst, after completion of the reaction carried out with metallic aluminum, the hydrocarbon layer was carefully poured off and immediately a fresh portion of reagents was added to the remaining complex and the mixture heated on a water bath. The reaction began at 50-55°, proceeded very energetically, and was complete in a few minutes. As the reaction mixture cooled, the complex compound again settled to the bottom of the flask and it could be used in reactions 3-4 times. Its amount gradually decreased due to its partial solubility in the reaction mixture. The results of this series of experiments are given in Table 3.

The ethylbenzene obtained had the following constants:

B. p. 135.5° (760 mm), n_D^{20} 1.4960, d_4^{20} 0.8664, MR_D 35.75. C_8H_{10}. Calc. 35.54.

The polyethylbenzenes distilled at 150-190°. They were not studied in more detail.

TABLE 3

No. of experiment	Ratio benzene : : ethyl bromide	Catalyst used	Yield of alkylation product (in %)	Composition of alkylation products (in %)	
				ethylbenzene	polyethylbenzene
1	3 : 1	0.01 g-atom of aluminum	46.0	90.9	9.1
2	3 : 1	Complex from Exp. 1	47.0	92.1	7.9
3	3 : 1	Complex from Exp. 2	38.5	79.3	20.7
4	4 : 1	0.01 g-atom of aluminum	46.4	93.0	7.0
5	4 : 1	Complex from Exp. 4	49.0	90.7	9.3
6	4 : 1	Complex from Exp. 5	45.0	79.6	20.4
7	4 : 1	Complex from Exp. 6	33.8	73.8	26.2
8	5 : 1	0.01 g-atom of aluminum	53.7	94.7	5.3
9	5 : 1	Complex from Exp. 8	57.7	80.0	20.0
10	5 : 1	Complex from Exp. 9	44.4	75.5	24.5
11	5 : 1	Complex from Exp. 10	36.4	67.9	32.1
12	6 : 1	0.01 g-atom of aluminum	68.4	95.0	5.0
13	6 : 1	Complex from Exp. 12	64.0	90.6	9.4
14	6 : 1	Complex from Exp. 13	56.8	88.4	11.6
15	6 : 1	Complex from Exp. 14	48.6	86.6	13.4
16	8 : 1	0.01 g-atom of aluminum	67.4	96.0	4.0
17	8 : 1	Complex from Exp. 16	48.8	85.2	14.8
18	8 : 1	Complex from Exp. 17	43.6	76.4	23.6

Alkylation of Benzene with n-Propyl Bromide

In this series of experiments mixtures were studied with molar ratios of benzene : n-propyl bromide of 4 : 1 and 6 : 1 with 0.01 g-atom of metallic aluminum. In the first case the yield of alkylation product was 54.3% (of this 88.5% was propylbenzene and 11.5% polypropylbenzene) and in the second, 76.5% (of this 92.3% was propylbenzene and 7.7% polypropylbenzene). With use of the complex the yield of alkylation products remained practically the same as when using metallic aluminum.

The reaction product distilled at 152-158° and was a mixture of propylbenzenes with isopropylbenzene predominating, as is obvious from the data in Table 4.

TABLE 4

Fractions and propylbenzenes	Weight of fraction (in %)	Boiling point (760 mm)	n_D^{20}	d_4^{20}	MR_D^*
I fraction	77.2	152-154°	1.4916	0.8618	40.40
II fraction	12.0	154-157	1.4916	0.8619	40.39
III fraction	6.5	157-158	1.4918	0.8619	40.39
Residue and losses	4.3	–	–	–	–
Isopropylbenzene [7, 8]	–	152.39	1.4915	0.8618	–
n-Propylbenzene [7, 8]	–	159.22	1.4920	0.8620	–

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* For C_9H_{12} calculated MR_D 40.16.

Alkylation of Benzene with n-Butyl Bromide

The experiments were carried out with 0.01 g-atom of metallic aluminum. The results are given in Table 5.

TABLE 5

Ratio benzene: : butyl bromide	Yield of butylbenzenes (in %)
3 : 1	56.2
4 : 1	70.0
5 : 1	79.3
6 : 1	83.7
8 : 1	81.9

On using the complex in an experiment with a component ratio of 6 : 1, the yield of butylbenzene was reduced to 65.1%. On distilling the reaction product, fractions were isolated with the constants given in Table 6.

Comparison of the data in Table 6 with literature data shows that the reaction product was a mixture of isobutylbenzenes.

SUMMARY

1. The complex compound formed in the alkylation of benzene with alkyl halides in the presence of metallic aluminum may be successfully used as catalyst for the same reaction.

TABLE 6

Fraction and butylbenzenes	Weight of fraction (in %)	Boiling point (760 mm)	n_D^{20}	d_4^{20}	MR^*_D
I fraction	21.9	168-172°	1.4919	0.8650	44.87
II fraction	29.0	172-173.5	1.4910	0.8640	44.92
III fraction	20.9	173.5-175	1.4909	0.8618	44.91
IV fraction	23.2	175-179	1.4905	0.8618	–
Residue and losses	5.0	–	–	–	–
n-Butylbenzene [9]	–	183.0	1.4897	0.8603	–
sec-Butylbenzene [9]	–	173.0	1.4898	0.8622	–
Isobutylbenzene [9]	–	172.8	1.4865	0.8535	–
tert-Butylbenzene [9]	–	169.5	1.4926	0.8666	–

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* For $C_{10}H_{14}$ calculated MR_D 44.78.

2. The alkylbenzene yield increased with increase in benzene content of the reaction mixture.

3. The alkylbenzene yield increased with increase in the molecular weight of the halogen derivative; under optimal conditions the yield of ethylbenzene was 68.5%, propylbenzene 76.5% and butylbenzene 83.7% (on halogen derivative taken).

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INVESTIGATIONS IN THE FIELD OF CONJUGATED SYSTEMS

LXVI. THE ACTION OF BENZOSULFODICHLORO- AND BENZOSULFODIBROMO-AMIDE ON ALCOHOL SOLUTIONS OF ISOPRENE

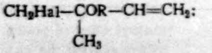
T. A. Zyryanova and A. A. Petrov

It was previously shown [1, 2] that piperylene, in contrast to divinyl [3], adds alkyl hypohalite to a considerable degree in the 1,4 position when treated with alcohol solutions of benzosulfodichloro- and benzosulfodibromoamides and, furthermore, regardless of the order of addition, the halogen fixation position is the fourth atom of the diene system. This characteristic of addition reactions of piperylene was explained by its high polarity.

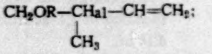
Isoprene, another close homolog of divinyl, has a lesser polarity ($\mu = 0.38 \cdot 10^{-18}$) [4]. It seemed interesting to compare the order of alkyl hypohalite addition to divinyl, piperylene and to this hydrocarbon under the same conditions.

There is data in the literature [5] on the order of methyl and ethyl hypochlorite addition to isoprene when methyl and ethyl alcohol solutions of isoprene are treated with tertiary butyl hypochlorite [5]. It was established that in both cases two products are formed: 2-alkoxy-1-chloro-2-methylbutene-3 and 4-alkoxy-1-chloro-2-methylbutene-2 in a ratio of 3:2. One of us had previously shown [6] that hypobromous acid (bromoamide method) adds to isoprene in the 1,2-position. The order of alkyl hypobromite addition was not investigated. Alkyl hypoiodite adds in the positions 1, 2 [6].

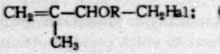
The following 6 isomeric haloethers would be expected from haloamide treatment of isoprene in alcohol.



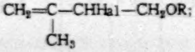
$CH_2Hal{-}\underset{CH_3}{\underset{|}{C}}OR{-}CH{=}CH_2;$ (I)



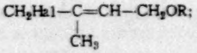
$CH_2OR{-}\underset{CH_3}{\underset{|}{C}}Hal{-}CH{=}CH_2;$ (II)



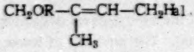
$CH_2{=}\underset{CH_3}{\underset{|}{C}}{-}CHOR{-}CH_2Hal;$ (III)



$CH_2{=}\underset{CH_3}{\underset{|}{C}}{-}CHHal{-}CH_2OR;$ (IV)



$CH_2Hal{-}\underset{CH_3}{\underset{|}{C}}{=}CH{-}CH_2OR;$ (V)



$CH_2OR{-}\underset{CH_3}{\underset{|}{C}}{=}CH{-}CH_2Hal.$ (VI)

Distillation of the methyl and ethyl chloroethers in vacuum showed that there were at least two substances differing sharply in boiling point. The one with the lower boiling point corresponded to 1,2-addition (I), the higher boiling one to 1,4-addition (V). This conclusion was reached without determining the chloroether structures as materials (I) and (V) had already been described in the literature [5]. In this case, the ratio of these chloroethers differed from that established earlier for other experimental conditions.

Distillation of the bromoethers gave evidence of the formation of only one substance. If we considered that the 1,4-product was any 10° fraction with a higher boiling point than that of the 1,2-product, then even under these conditions the amount of 1,4-product could not be more than 5% of the mixture.

We deduced the structure of the haloethers obtained from their behavior with alcoholic alkali and hydrogenation under pressure over Raney nickel.

Ethers with Formula (1) would be inert to alkali as their halogen is not conjugated with the diene system and is shielded by the alkoxyl group (vicinal effect). The ethers with formulas II, IV, V and VI would be expected to form diethers of unsaturated glycols very readily with or without allylic rearrangement. Haloethers with Formula (III) would give diene ethers of enolic character, which would form methylisopropylketone on hydrolysis.

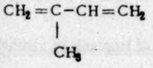
Actually, we found exceptionally low lability of the chlorine atom in the chloroether fractions corresponding to 1,2-addition of alkyl hypochlorites. Only 7.34 and 5.79%, respectively, of total chlorine in the chloroether sample, passed into solution on heating corresponding fractions of methyl and ethyl chloroethers with a 3-fold excess of alcoholic alkali for 10 hours. The chloroethers were extracted from the reaction mixture practically unchanged. A small initial fraction of alkali-treated chloroethers contained a certain amount of enol ether, which possibly corresponded to the 3,4-addition of hypochlorites, as it partially dissolved in 5% H_2SO_4 in the cold with the formation of a carbonyl compound, possibly, methyl isopropyl ketone; however, its amount was so small that the 3,4-products could be said to be practically absent. Their amount did not exceed 2-3%.

The chloroether fractions, corresponding to 1,4-addition, readily lost the halogen to form the corresponding isoprene-glycol diethers.

The bromoethers remained inert to alcoholic alkali. Only 8.1% of the bromine in the sample went into solution on heating the methyl bromoether with a 3-fold excess of alcoholic alkali for 10 hours. The initial fraction of alkali-treated bromoether, also contained a minute amount of enol ether, but the amount of 3,4-isomer in the mixture was not greater than 2-3%.

Only the allyl halides were affected by hydrogenation over Raney nickel under pressure and at room temperature. In the absence of such halide atoms the double bond, if it exists in the compound, is hydrogenated. Therefore, of the 6 possible haloethers, (I) and (III) should give saturated haloethers when hydrogenated; the rest should give unsaturated ethers not containing halogen.

Only hydrogenation of the double bond occurred when the chloroether fraction obtained by us (corresponding to 1,2-addition) was hydrogenated over Raney nickel. The chlorine was practically untouched. The methyl ether of prenyl alcohol was formed by hydrogenating the chloroether fraction corresponding to 1,4-addition under the same conditions.

Material	Percent of 1,4-products		Dipole moment $\mu \cdot 10^{18}$ [4]
	ROCl	ROBr	
$CH_2=CH-CH=CH_2$	10	0	0
 $CH_2=C(CH_3)-CH=CH_2$	30	5	0.38
$CH_3-CH=CH-CH=CH_2$	45	20	0.68

Hydrogenation of the bromoethers over nickel gave practically no unsaturated ethers. Hydrogenation of the double bond occurred. The amounts of lower-boiling fractions which could be obtained by distilling the reduced product indicate the presence of other isomers, besides (I), in amounts not greater than 5%.

Thus, it was established that, under the conditions chosen by us, 1,2- and 1,4-chloroethers were obtained in a ratio of 2:1 with methyl hypochlorite and in a ratio of 2.4:1 for ethyl hypochlorite, in addition of alkyl hypochlorite to isoprene. A decrease in the amount of 1,4-products in changing from methyl to ethyl alcohols was also observed in analogous divinyl reactions [3].

1,2-Bromoethers are almost the only ones obtained in addition of alkyl hypobromite to isoprene.

Data on the order of alkyl hypohalite addition to divinyl, isoprene and piperylene under approximately the same conditions are compared in the table.

It can be seen from the table that the amount of 1,4-products increases with increase in polarity of the hydrocarbons. This may be explained by an increase in reaction capacity of the 1,4-position as well as by an increase in the tendency of hydrocarbons to form a transitional eight-membered complex due to the enhanced reaction between the 1st and 4th positions.

EXPERIMENTAL

The Action of Benzosulfodichloroamide on Isoprene in Methyl Alcohol

120 g of benzosulfodichloroamide (95-98% purity on active chlorine) was added in small portions over 3 hours to a mechanically stirred solution of 136 g (200 ml) of isoprene in 600 ml of methyl alcohol at 3-5°. Stirring was continued for a further 2 hours, after which the solution was left to stand until practically all the active chlorine had disappeared. The reaction products were distilled in steam. 145 g of an oil was obtained and excess isoprene was distilled off from this on a water bath using a fractionating column. The residue (80 g) was distilled at 50 mm with a Widmer column. The following fractions were obtained: 1st up to 50°, 6.2 g; 2nd 50-60°, 1.2 g; 3rd 60-63°, 1.4 g; 4th 63-66°, 40 g; 5th 66-70°, 4.3 g; 6th 70-80°, 1.1 g; 7th 80-85°, 1.8 g; 8th 85-90°, 20.7 g; 9th 90-95°, 1.4 g; residue, 6.0 g.

On distilling for the second time, the 4th fraction almost completely came over at 64-65° (50 mm).

d_4^{20} 1.0044, n_D^{20} 1.4450, MR 35.67. $C_6H_{11}OCl$. Calc. 35.95.

Found %: Cl 26.12, 26.00; OCH_3 23.00, 22.69. $C_5H_8OCH_3Cl$. Calculated %: Cl 26.34; OCH_3 23.05.

Literature data for chloroether (I) [5]: b. p. 68-69° (55 mm), n_D^{20} 1.4432.

33 g of material was heated with a solution of 42 g of KOH (threefold excess) in 200 ml of methyl alcohol for 10 hours. 0.638 g of chlorine was passed into the solution. By the usual method of working up the mixture, 28 g of unchanged chloroether was obtained:

B. p. 143-144° (759 mm); 64-65° (50 mm); d_4^{20} 1.0041, n_D^{20} 1.4448.

The first fraction of this chloroether (0.6 g) partially dissolved in 5% H_2SO_4. The solution gave a positive reaction for carbonyl compounds with p-nitrophenylhydrazone.

A solution of 12.6 g of the material in 150 ml methanol was hydrogenated at 20° C in presence of 8.5 g Raney nickel (paste) and 20 g of $CaCO_3$. The initial pressure was 78 atm. When the pressure stopped falling, the mixture was stirred in the autoclave for a further 2 hours and then diluted with water. The reaction product distilled off with water and alcohol and was separated from the distillate with saturated $CaCl_2$ solution. This yielded 8 g of material, which was separated into the following fractions by distillation: 1st 140-143°, 1 g; 2nd 143-144°, 5.5 g; 3rd 144-145°, 1.0 g.

For the 2nd fraction d_4^{20} 0.9915, n_D^{20} 1.4362.

Constants given in the literature for 1-chloro-2-methoxy-2-methylbutane [5]: b. p. 67-68° (55 mm), n_D^{22} 1.4313.

As the chloroether obtained was unsaturated, it was brominated with a chloroform solution of bromine at room temperature until the color persisted for 0.5 hours in the solution. At the beginning it was necessary to cool the mixture. 2 g of bromine were taken up by 5.1 g of material (2nd and 3rd fractions), which corresponded to a 33% content of unsaturated chloroether. After separation from the chloroform and the bromination products, the saturated chloroether had constants which were closer to the literature data.

B. p. 46.5-47° (20 mm), 67-68° (55 mm), 143-144° (762 mm); d_4^{20} 0.9932, n_D^{20} 1.4345.

Found %: Cl 26.11; OCH_3 22.48. $C_5H_{10}OCH_3Cl$. Calculated %: Cl 26.00; OCH_3 22.71.

The 8th fraction was used for further work without additional distillation: d_4^{20} 1.0065, n_D^{20} 1.4572.

Found %: Cl 24.82; OCH_3 24.00. $C_5H_8OCH_3Cl$. Calculated %: Cl 26.34; OCH_3 23.05.

Constants given in the literature for chloroether V [5]: b. p. 89-91° (55 mm), n_D^{20} 1.4595.

10 g of material was heated with excess KOH (12 g) in methyl alcohol. A precipitate of KCl immediately separated out. 2.127 g of chlorine (80.8%) was passed into the solution. The reaction mixture was extracted with ether (the ether solution was washed with saturated $CaCl_2$ solution) to yield about 6 g of 2-methyl-buten-2-diol-1,4 dimethyl ether.

B. p. 44-46° (10 mm), d_4^{20} 0.9117, n_D^{20} 1.4348.

Literature data [7]: b. p. 44-44.5° (10 mm), d_4^{20} 0.9096, n_D^{20} 1.4334.

By hydrogenating 5 g of the 8th fraction in 100 ml of methyl alcohol in the presence of 7.0 g of Raney nickel (paste) and 20 g of $CaCO_3$, with an initial pressure of 80 atm, we obtained 2.3 g of material, the greater part of which boiled at 100-105°, d_4^{20} 0.7902, n_D^{20} 1.4100.

Literature data for the methyl ester of prenyl alcohol [5]: b. p. 102-104.5°, n_D^{25} 1.4119.

The Action of Benzosulfodichloroamide on Isoprene in Ethyl Alcohol

By the action of 120 g of benzosulfodichloroamide on a solution of 200 ml of isoprene in 550 ml of ethyl alcohol under the conditions described in the previous experiment, 74 g of an oil was obtained, which was separated into the following fractions by distillation at 50 mm: 1st 30-60°, 10 g; 2nd 60-70°, 2.8 g; 3rd 70-80°, 38.5 g; 4th 80-100°, 6.1 g; 5th 100-105°, 15.1; residue 11.2 g.

On distilling for the second time, the greater part of the 3rd fraction came over at 72-74° (21 g).

d_4^{20} 0.9742, n_D^{20} 1.4420, MR 40.37. $C_7H_{13}OCl$. Calc. 40.57.

Found %: Cl 24.30, 24.10; OC_2H_5 29.80. $C_5H_8OC_2H_5Cl$. Calculated %: Cl 23.86; OC_2H_5 30.32.

Literature data for the ethyl chloroether (I) [5]: b. p. 74-77° (55 mm), n_D^{20} 1.4395.

22 g of the 3rd fraction was boiled for 10 hours with a threefold excess of KOH (24 g) in 100 ml of ethyl alcohol and 0.319 g of chlorine was passed into the solution. 18.2 g of chloroether was isolated from the reaction mixture; 13.4 g of pure ether with b. p. 72-74° (50 mm) was obtained.

d_4^{20} 0.9712, n_D^{20} 1.4410, MR 40.41. $C_7H_{13}OCl$. Calc. 40.57.

The 1st fraction (0.5 g) as in the previous experiment, contained enol ether. The 5th fraction had d_4^{20} 0.9907, n_D^{20} 1.4582 and was used without additional purification.

Found %: Cl 24.51, 24.76; OC_2H_5 29.01, 29.80. $C_5H_8OC_2H_5Cl$. Calculated %: Cl 23.86; OC_2H_5 30.32.

Literature data for ethyl chloroether (V) [5]: b. p. 69-71° (10 mm), n_D^{20} 1.4575.

10 g of fraction 5 was boiled for 10 hours with a threefold excess of KOH (12 g) in 50 ml of ethyl alcohol and 2.216 g of chlorine (84.1%) was passed into the solution. 7.5 g of 2-methyl-buten-2-diol-1,4 diethyl ether with b. p. 63-65° (10 mm), d_4^{20} 0.8752, n_D^{20} 1.4328.

Literature data [7]: b. p. 63.5-64° (10 mm), d_4^{20} 0.8885, n_D^{20} 1.4340.

The Action of Benzosulfodibromoamide on Isoprene in Methyl Alcohol

The product obtained by the usual method from 200 ml of isoprene in 500 ml of methyl alcohol and 190 g of benzosulfodibromoamide, was separated into the following fractions by distillation at 18 mm: 1st 50-60°, 4.7 g; 2nd 60-63°, 107 g; 3rd 63-70°, 7.2 g; residue, 10.1 g. 3.2 g of the residue distilled at 135-145°.

For the main material b. p. 62-64° (20 mm), d_4^{20} 1.2803, n_D^{20} 1.4706.

Found %: Br 42.93, 42.74; OCH_3 18.20, 18.31. $C_5H_8OCH_3Br$. Calculated %: Br 44.63; OCH_3 17.33.

The low halogen content of the bromoether obtained may be due to treating the mixture with steam. However, another method of isolating the bromoether (extraction with ether) did not give a material of greater purity.

The fraction 135-145° (20 mm) was also analyzed.

Found %: Br 54.05, 54.36. $C_5H_8[OCH_3]_2Br_2$. Calculated %: Br 55.11.

According to the analytical data this fraction was the slightly impure product of the addition of 2 molecules of methyl hypobromite to 1 molecule of isoprene.

53 g of bromoether (fraction 60-70°) was heated with 50 g (3-fold excess) of KOH in 150 ml of methyl alcohol for 10 hours. 1.918 g of bromine was passed into the solution. The reaction product (45 g) was distilled in vacuum. At 125 mm, 0.4 g of low boiling material distilled off. On further lowering the pressure to 20 mm, the following fractions were obtained: 1st 60-62°, 4.8 g; 2nd 62-62.5°, 37.5 g; residue, 0.5 g.

The main material had the constants:

B. p. 62-62.5° (20 mm), d_4^{20} 1.2941, n_D^{20} 1.4726, MR 38.79. $C_6H_{11}OBr$. Calc. 38.85.

Found %: Br 44.31; OCH_3 16.94. $C_5H_8OCH_3Br$. Calculated %: Br 44.63; OC_2H_5 17.33.

Hydrogenating the same fraction of methyl bromoether (I) (30 g) in methyl alcohol (150 ml) in the presence of Raney nickel (15 g of paste) and $CaCO_3$ (30 g) with an initial pressure of 80 atm, gave 21 g of reaction product, which was separated into the following fractions by distillation in vacuum: 1st about 40° (120 mm), 0.5 g and more at (20 mm); 2nd up to 60°, 2.5 g; 3rd 60-60.5°, 16 g; residue, 1.0 g.

Found for the 1st fraction: b. p. 100-110°, n_D^{20} 1.4180.

For the 3rd fraction d_4^{20} 1.2751, n_D^{20} 1.4630. This fraction was brominated in chloroform. 13 g of material took up about 2.6 g of bromine, which corresponded to a 20% content of unsaturated (original) ether. After distillation of the ether and separation from the bromination products, the material had the following constants:

B. p. 62°, d_4^{20} 1.2777, n_D^{20} 1.4595, MR 38.78. $C_6H_{13}OBr$. Calc. 39.32.

Found %: Br 43.98; OCH_3 17.42. $C_5H_{10}OCH_3Br$. Calculated %: Br 44.13; OCH_3 17.13.

The Action of Benzosulfodibromoamide on Isoprene in Ethyl Alcohol

The product obtained in the usual way from 100 ml of isoprene in 250 ml of ethyl alcohol and 95 g of dibromoamide, was separated into the following fractions by distillation at 15 mm: 1st up to 62°, 7.9 g; 2nd 62-63°, 36 g; 3rd 63-67°, 3.3 g; 4th 67-80°, 1.5 g; 5th 80-85°, 2.4 g; 6th 85-100°, 1.2 g; 7th 100-125°, 1.5 g; residue 7.2 g.

For the fraction 62-63° (15 mm)

d_4^{20} 1.2335, n_D^{20} 1.4651, MR 43.28. $C_7H_{13}OBr$. Calc. 43.47.

Found %: Br 41.30, 41.90; OC_2H_5 23.06, 23.66. $C_5H_8OC_2H_5Br$. Calculated %: Br 41.39; OC_2H_5 23.34.

For the fraction 80-85° (15 mm)

d_4^{20} 1.1110, n_D^{20} 1.4638.

Found %: Br 29.42, 29.52; OC_2H_5 32.09, 32.50.

The bromoether fractions 62-100° (42 g) were hydrogenated in 150 ml of methyl alcohol in the presence of 20 g of Raney nickel (paste) and 20 g of $CaCO_3$, with an initial pressure of 80 atm. 39 g of material was obtained, which was separated into the following fractions by distillation: 1st up to 60° at 120 mm, 0.5 g and more at 20 mm; 2nd up to 69°, 2.0 g; 3rd 69-70°, 31.5 g; residue 2.7 g.

For the fraction 69-70° (20 mm) d_4^{20} 1.2059, n_D^{20} 1.4528.

On brominating 21 g of this fraction, 1.8 g of bromine was taken up, which corresponded to a 9% unsaturated bromoether content. When separated from the chloroform and the bromination products, the saturated bromoether had the constants:

B. p. 68° (20 mm), d_4^{20} 1.2100, n_D^{20} 1.4522, MR 43.52. $C_7H_{15}OBr$. Calc. 43.93.

Found %: Br 41.02; OC_2H_5 22.95. $C_5H_8OC_2H_5Br$. Calculated %: Br 40.96; OC_2H_5 23.10.

SUMMARY

1. The action of benzosulfodichloroamide and benzosulfodibromoamide on isoprene in methyl and ethyl alcohols was investigated.

2. It was shown that in the first case alkyl hypochlorites add in the 1,2- and 1,4-positions. The ratio of these isomeric chloroethers is 2-2.4 : 1. In both cases the predominating fixation position of the halogen is the first carbon atom of the diene system. The third possible isomer – the 3,4-product – is obtained in minute quantities.

3. It was established that alkyl hypobromites add to isoprene almost exclusively in the 1,2-position. Not more than 5% of 1,4-bromoethers are formed. There is an insignificant amount of 3,4-bromoethers.

4. It was shown that the order of alkyl hypohalite addition depends on the polarity of the original diene hydrocarbon. Increase in polarity is conducive to 1,4-addition.

5. Methyl and ethyl ethers of 1-chloro- and 1-bromo-2-methylbutanol-2 are obtained by hydrogenating the products of hypohalite addition to isoprene in the 1,2-position.

6. Dimethyl and diethyl ethers of 2-methyl-buten-2-diol-1,4 are obtained by alcoholic alkali treatment of 1,4-chloroethers.

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SYNTHESIS OF HYDROCARBONS

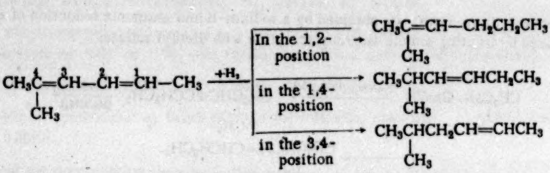
LVII. PARTIAL REDUCTION OF HYDROCARBON DIENES WITH CONJUGATED DOUBLE BOND SYSTEMS USING SODIUM IN LIQUID AMMONIA

R. Ya. Levina, V. R. Skvarchenko, M. G. Kuzmin and E. G. Treshchova

It was previously shown [1-4] that in the reduction of conjugated diene hydrocarbons by sodium in liquid ammonia, the mode of addition of hydrogen to the conjugated diene system varies with the structure of the original diene. In alkadienes of symmetrical structure,reduction can proceed only in two ways – either in the 1,2- or 1,4-position; it was shown that the greater the number of radicals on each end carbon atom of the conjugated system the greater the degree of addition in the 1,2-position.

Alkadienes of unsymmetrical structure whose 1,2- and 3,4-positions are not equivalent, may add hydrogen in three ways – at the ends of the conjugated system (1,4) and directly to each of the double bonds (1,2 and 3,4). Up to now, the partial reduction of diene hydrocarbons of unsymmetrical structure (which could add hydrogen in three ways) by sodium in liquid ammonia has been studied by us for only one example – 2-methylpentadiene-2,4. On reducing this hydrocarbon, which has a free methyl group, with sodium in liquid ammonia, 93-94 % of the hydrogen addition occurred in the 1,4-position and 6-7% in the 1,2-position (at the vinyl radical); hydrogen did not add in the 3,4-position (at the isocrotyl radical) [4].

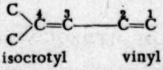
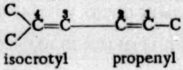
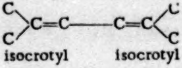
In this work we studied the partial reduction by sodium in liquid ammonia of 2-methylpentadiene-2,4, which also has an unsymmetrical structure. Examination of the combination scattering spectrum of the reaction product showed that in this case, hydrogen addition to the conjugated system occurred in the three possible ways: in the 1,2-position, with the formation of 2-methylhexene-2 (~ 12 %), in the 1,4-position, with the formation of 2-methylhexene-3 (~43%) and in the 3,4-position with the formation of 2-methylhexene-4 (~45%):



Thus, 2-methylhexadiene-2,4 adds hydrogen not only in the 1,4-position but also directly to each of the two double bonds, i.e., to the isocrotyl radical (in the 3,4-position) in which the double bond is activated by two methyl groups and to the propenyl radical (in the 1,2-position) in which the double bond is activated by one methyl group.

It seemed interesting to compare the results of the partial reduction by sodium in liquid ammonia of three diene hydrocarbons (2-methylpentadiene-2,4 [4], 2-methylhexadiene-2,4 and 2,5-dimethylhexadiene-2,4 [1]) in which one of the radicals is isocrotyl, while the second is vinyl, propenyl and isocrotyl, respectively; as illustrated in Table 1, the behavior of the hydrocarbons in this reaction varies with the structure of the second radical.

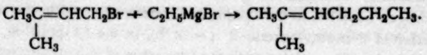
TABLE 1

No.	Diene hydrocarbons		Hydrogen addition at the "separation moment" (sodium in liquid ammonia) (in %)		
	Name	Formula	in the 1,4-position	in the 3,4-position	in the 1,2-position
(I)	2-Methylpentadiene-2,4		∞ 93—94	0	∞ 6—7%
(II)	2-Methylhexadiene-2,4		∞ 43	∞45	∞ 12%
(III)	2,5-Dimethylhexadiene-2,4		0	100	(the 1,2-position is equal to the 3,4-position)

Naturally, the transfer of the reaction center, i.e. reduction in the 1,4-position, occurs to a greater degree in hydrocarbon (I) (which does not have the counter effect of the methyl group at the first carbon atom in the conjugated system) than in hydrocarbon (II), while it does not occur at all in hydrocarbon (III).

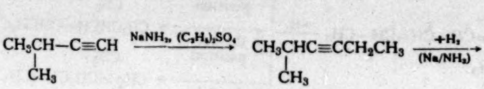
For qualitative and quantitative determination of the composition of the mixture of the three hydrocarbons obtained (on the reduction of 2-methylhexadiene-2,4) by the combination light-scattering spectra, we synthesized these hydrocarbons by methods which excluded all doubt on the position of the double bond in them.

Thus, 2-methylhexene-2 was obtained by treating isoprene hydrobromide with ethylmagnesium bromide:



$$\underset{\displaystyle CH_3}{CH_3\overset{}{C}}{=}CHCH_2Br + C_2H_5MgBr \rightarrow \underset{\displaystyle CH_3}{CH_3\overset{}{C}}{=}CHCH_2CH_2CH_3.$$

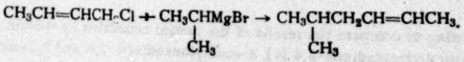
2-Methylhexene-3 (trans-form) was obtained by a sodium-liquid ammonia reduction of ethylisopropylacetylene, synthesized by treating sodium isopropylacetylide with diethyl sulfate:



$$\underset{\displaystyle CH_3}{CH_3CH}{-}C{\equiv}CH \xrightarrow{NaNH_2,\ (C_2H_5)_2SO_4} \underset{\displaystyle CH_3}{CH_3CH}C{\equiv}CCH_2CH_3 \xrightarrow[(Na/NH_3)]{+H_2}$$

$$\longrightarrow \underset{\displaystyle CH_3}{CH_3CH}CH{=}CHCH_2CH_3.$$

2-Methylhexene-4 was synthesized by treating divinyl hydrochloride with isopropylmagnesium bromide:



$$CH_3CH{=}CHCH_2Cl + \underset{\displaystyle CH_3}{CH_3CH}MgBr \rightarrow \underset{\displaystyle CH_3}{CH_3CH}CH_2CH{=}CHCH_3.$$

As divinyl hydrochloride could react with the organomagnesium compound as the secondary chloride ($CH_3CHClCH=CH_2$), the hydrocarbon obtained could have contained a trace of the isomer 2,3-dimethylpentene-4 (the alkene with the double bond in the α-position). However, an examination of the combination scattering spectrum of the 2-methylhexene-4 showed that it did not contain this impurity (absence of the 1640 cm^{-1} frequency in the spectrum).

EXPERIMENTAL

Synthesis of 2-Methylhexadiene-2,4 and Its Possible Partial Hydrogenation Products – Isomeric 2-Methylhexenes

2-Methylhexadiene-2,4 was prepared by catalytic isomerization of 2-methylhexadiene-1,5 (b. p. 86.5-87° at 740 mm, n_D^{20} 1.4194, d_4^{20} 0.7204), synthesized by treating a mixture of allyl chloride and methylallyl chloride in ether with magnesium; the isomerization was carried out over chromic oxide on aluminum oxide at 250° in a slow stream of nitrogen (rate of flow of hydrocarbon, 0.15 ml per minute). After distilling the catalysate over sodium through a column, 2-methylhexadiene-2,4 (67%) was isolated:

B. p. 110.5° (743 mm), n_D^{20} 1.4690, d_4^{20} 0.7457.

Literature data [5]: b. p. 111.5° (760 mm), n_D^{20} 1.4680, d_4^{20} 0.7449.

2-Methylhexene-2 was prepared by treating isoprene hydrobromide with ethylmagnesium bromide using the method developed by us earlier [6]:

b. p. 94-94.5° (755 mm), n_D^{20} 1.4127, d_4^{20} 0.7100, MR_D 34.46. C_7H_{14}. Calc. 34.06.

Literature data [7]: b. p. 95.4° (760 mm), n_D^{20} 1.4103, d_4^{20} 0.7081.

2-Methylhexene-3. Isopropylacetylene (8.9 g, 60%) was prepared by heating 3,4-dibromo-2-methylbutane* (50 g) at 260-270° with molten caustic soda (100 g) in dry kerosene.

An ether solution of isopropylacetylene (17 g, 0.25 mole) was gradually added to sodamide (13 g, 0.33 mole) in absolute ether, while the reaction mixture was continuously stirred. The reaction mixture was heated on a water bath until ammonia was no longer evolved, then freshly distilled diethyl sulfate (43 g, 0.23 moles) was added gradually and heating was continued for 25-30 hours; the reaction mixture was decomposed with water. The residue, obtained after distilling off the ether from a washed and dried (calcium chloride) ether extract, gave ethylisopropylacetylene (7.9 g, 53 %) on distillation on a column:

b. p. 93° (738 mm), n_D^{20} 1.4143, d_4^{20} 0.7352, MR_D 32.72. C_2H_{12}. Calc. 32.52.

Literature data [8]: b. p. 94-95° (760 mm), n_D^{20} 1.4114, d_4^{20} 0.7263.

Reduction of ethylisopropylacetylene (7.4 g, 0.076 mole) with sodium (12 g, 0.5 mole) in liquid ammonia (200 ml) at a temperature of −60° to −70° with stirring for 5 hours, gave 2-methylhexene-3 (4.5 g, 60%):

b. p. 84.1° (743 mm), n_D^{20} 1.3999, d_4^{20} 0.6892, MR_D 34.52.

2-Methylhexene-3, synthesized by Boord [9], had the following constants: b. p. 85.6-86.1° (760 mm), n_D^{20} 1.3991, d_4^{20} 0.6942.

Investigation of the combination light scattering spectrum of this hydrocarbon, showed that it was the pure trans-form (frequency 1668 cm^{-1}).

2-Methylhexene-4. An ether solution of divinyl hydrochloride was added to isopropylmagnesium bromide with continuous stirring; the reaction mixture was heated for 2 hours and decomposed with 10% acetic acid. After the usual working up of the reaction mixture, evaporation of the ether and distillation of the hydrocarbon residue over sodium through a column, 2-methylhexene-4 (18%) was obtained:

b. p. 86.5-87° (746 mm), n_D^{20} 1.4040, d_4^{20} 0.7030, MR_D 34.15.

Literature data [10], b. p. 86.9° (760 mm), n_D^{20} 1.4045, d_4^{20} 0.7025.

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* 3,4-Dibromo-2-methylbutane (b.p. 85-87° at 25 mm, n_D^{20} 1.5100) was prepared by bromination of isoamylene, free from traces of trimethylethylene (the isoamylene was prepared by pyrolysis of isoamylacetate at 500° in a stream of nitrogen).

In the spectrum of the 2-methylhexene-4 synthesized, the frequencies 1658 (1) and 1668 (14) were found in the region of 1600 cm^{-1}; this showed that the hydrocarbon was a mixture of cis- (~ 7 %) and trans-forms (~ 93%).

Partial Reduction of 2-Methylhexadiene-2,4 with Sodium in Liquid Ammonia

An ether solution of 2-methylhexadiene-2,4 (22 g, 0.22 mole) was added with continuous stirring to a solution of sodium (38 g, 1.65 moles) in liquid ammonia (300 ml), cooled to −60 to −70° (solid carbon dioxide in alcohol). Stirring was continued for 4 more hours with cooling, then absolute ether (300 ml) was added and the reaction mixture was left overnight at room temperature to evaporate the ammonia. Next day the excess sodium was destroyed by careful addition of water (under ether). After evaporation of the ether from the washed and dried (calcium chloride) ether extract, the residue was distilled over sodium; it boiled over a wide range, 85.4-96° (774 mm). The total yield of the mixture of alkenes (2-methylhexenes with the double bond in various positions) – the possible products of partial hydrogenation of 2-methylhexadiene-2,4 – was 12 g (53.5%). Fractional distillation of this hydrocarbon mixture on a column, gave fractions, whose compositions were investigated by combination light scattering. The results obtained are given in Table 2.

TABLE 2

Fraction No.	Boiling point at 760 mm	Wt. (% total reaction product)	Composition (in %)		
			2-Methylhexene-3	2-Methylhexene-4	2-Methylhexene-2
1	85.4—85.6°	16	100 (80% trans-form 20% cis-form	—	—
2	85.6—86.6°	34	65	35	—
3	86.6—88.5°	25	~20—25	~75—80	—
4	88.5—92.5°	14	—	70	30
5	92.5—96°	11	—	30	70

Calculation of the composition of the total reduction product from this data, showed that the mixture of alkenes obtained contained ~43% of 2-methylhexene-3, ~45% of 2-methylhexene-4 and ~ 12% of 2-methylhexene-2.

SUMMARY

1. The partial reduction of 2-methylhexadiene-2,4 by sodium in liquid ammonia was studied. It was shown that the reduction proceeded in three possible ways – in the 1,2- (~ 12 %), in the 1,4- (~43 %) and in the 3,4-position (~45 %). The composition of the 2-methylhexene mixtures formed was determined by combination light scattering.

2. The synthesis is described of the trans-form of 2-methylhexene-3 (by reduction of 2-methylhexene-3 using sodium in liquid ammonia) and 2-methylhexene-4 (by treatment of divinyl hydrochloride with isopropylmagnesium bromide).

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INVESTIGATIONS IN THE FIELD OF UNSATURATED CYCLIC HYDROCARBONS AND THEIR DERIVATIVES

XXII. THE PROBLEM OF THE STERIC STRUCTURE OF BICYCLO-(0,2,2)-HEXANE

N. A. Domnin

Chemists and physicists have devoted numerous investigations to the stereochemistry of various deformed organic molecules and interest in this field is still increasing. Bicyclo-(0,2,2)-hexane, first synthesized by N. D. Zelinsky and K. A. Kochetkov [1], is one of the most characteristic and clear examples of deformed molecules.

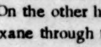
The chair form, which is generally recognized as the preferred and more stable form of cyclohexane, cannot be taken as the starting structure from which bicyclo-(0,2,2)-hexane is synthesized. The formation of bicyclo-(0,2,2)-hexane from it faces such great and obvious steric hindrance that it can be eliminated straight away. On the other hand, it is easily seen that the formation of bicyclo-(0,2,2)-hexane from the boat form of cyclohexane through the bonding of the 1st and the 4th carbon atoms in the cis-position, faces considerably lesser steric hindrance. However, as we have shown in [2], even in this case the difficulties are still great.

Therefore, we consider that if bicyclo-(0,2,2)-hexane exists, it exists in the steric form of a bicyclic structure, formed by two four-membered rings, bonded together in the cis-position, exactly in the same way as the two six-membered rings of cis-decalin.

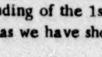
Linstead, Berret, Meade and Cook [3] synthesized cis- and trans-bicyclo-(0,3,3)-octane and showed that its cis-form was obtained with relative ease and in good yields, while the trans-form was obtained only with a great deal of work and in insignificant yields. The authors considered that the cis-form was hardly deformed (formed without distortion of the valency angles) while the trans-form is considerably deformed, with distortion of the valency angles of more than 70°.

There is good reason to conclude that bicyclo-(0,2,2)-hexane is also formed similarly to decalin and bicyclo-(0,3,3)-octane.

If such an assumption is made, then bicyclo-(0,2,2)-hexane must also exist in the cis- and trans-forms, whose steric structure may be expressed by the following models:



Cis-form



Trans-form

However, the difference in the degree of deformation (tension) between bicyclo-(0,2,2)-hexane and bicyclo-(0,3,3)-octane would be quite substantial. While the cis-form of bicyclo-(0,3,3)-octane is hardly deformed, the cis-form of bicyclo-(0,2,2)-hexane must have considerable distortion of the valancy angles. However, this distortion would not be greater than the distortion of the valancy angles in the trans-form of bicyclo-(0,3,3)-octane.

From this it seems possible that the cis-form of bicyclo-(0,2,2)-hexane would be capable of existing and that possibly the hydrocarbon of N. D. Zelinsky and K. A. Kochetkova is the cis-form of bicyclo-(0,2,2)-hexane considered here, with the steric structure shown. In any case, the steric model suggested here for cis-bicyclo-(0,2,2)-hexane, being much less deformed, is more probable than the more deformed model of a six-membered ring with a bridge in the cis-position of the 1st and 4th carbon atoms.

The molecule of the trans-form of bicyclo-(0,2,2)-hexane would be, as the models show, extremely deformed and, probably, would be unable to exist at all.

It may be concluded from the above discussion on the form of bicyclo-(0,2,2)-hexane that the synthesis of its cis-form could more readily be achieved by using the same methods as for the synthesis of cis- and trans-bicyclo-(0,3,3)-octane, namely, by completing two four-membered rings from the corresponding cis-derivatives of an open chain.

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REACTIONS OF FREE RADICALS IN SOLUTION

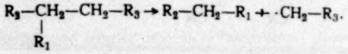
V. DESTRUCTION OF POLYMERIC MOLECULES BY FREE RADICALS

S. E. Bresler, B. A. Dolgoplosk, V. A. Krol and S. Ya. Frenkel

The majority of the free radical reactions described in the literature are chemical conversions where the radical splits off a hydrogen or halide atom from the solvent [1].

$$R_1\cdot + X - R_2 \rightarrow R_1 - X + R_2\cdot. \qquad (1)$$

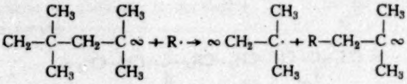
At the same time, similar reactions where a carbon-carbon bond in organic compounds was broken, have been studied in only a few cases. Thus, for example, A. L. Klebansky and L. P. Fomina established that the diallyl bond in complex organic molecules was broken by free radicals [2]. B. A. Dolgoplosk, E. I. Tinyakova and V. N. Reikh established that oxidation-reduction systems, which are sources of free radicals, cause the destruction of polyisobutylene and other polymers in hydrocarbon media [3, 19]. It must be noted that such reactions were generally considered as very unlikely until lately, as in this case the radical attack occurs not through breaking of the bond (1), but at the "side".



$$R_2-\underset{R_1}{CH_2}-CH_2-R_3 \rightarrow R_2-CH_2-R_1 + \cdot CH_2-R_3. \qquad (2)$$

In such a mechanism, the formation of a transition complex is hindered and the activation energy of the process is increased.*

It was shown in a previous report** that free aliphatic and aromatic radicals ($CH_3\cdot$, $C_2H_5\cdot$, $C_6H_5\cdot$, $C_6H_5-C_6H_4\cdot$ etc.), formed by decomposition of corresponding diazoamino compounds, cause gel formation in concentrated benzene solutions of natural rubber. At the same time, a considerable decrease in viscosity is observed under analogous conditions in solutions of polyisobutylene, which does not have double bonds. This was explained by the reaction of the free radicals with the weakened carbon-carbon bond by the following scheme:



$$CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}\infty + R\cdot \rightarrow \infty CH_2-\underset{CH_3}{\overset{CH_3}{C}}\cdot + R-CH_2-\underset{CH_3}{\overset{CH_3}{C}}\infty \qquad (3)$$

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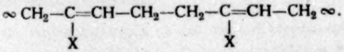
* See [1], p. 73.

** See [2], p. 810.

It seemed likely that this reaction was not specific for polyisobutylene but occurred in the case of any polymers with weakened carbon-carbon bonds, for example, polymers of isoprene, divinyl and other dienes, containing diallyl grouping of the atoms in the chain:



$$\sim CH_2{-}\underset{\displaystyle X}{\underset{|}{C}}{=}CH{-}CH_2{-}CH_2{-}\underset{\displaystyle X}{\underset{|}{C}}{=}CH{-}CH_2 \sim. \qquad (4)$$

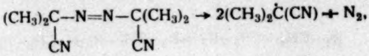
In this case the reaction of free radicals with the polymeric molecules would be expected to develop in two competing directions: a) "sewing together" of polymeric chains, resulting in an increase in the viscosity of the solution and in gel formation, and b) polymer destruction due to the breaking of carbon-carbon bonds:

$$R\cdot + \sim CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH \sim \rightarrow \sim CH{=}CH{-}CH_2\cdot + R{-}CH_2{-}CH{=}CH \sim. \qquad (5)$$

Apparently, the proportion of the reaction leading to the build-up of the polymer must fall with a decrease in the concentration of the solution. While, on the contrary, the degree of destruction of polymeric chains, which is not due to intermolecular reactions of the latter, should appear in a more "pure" form in sufficiently dilute solutions.

The reactions of some free radicals with polymers of different structure and over a wide range of concentrations were studied in the present work. Alkylphenyltriazene and azoisobutyric dinitrile which decompose on heating to form alkyl and dimethylcyanomethyl radicals, were selected as sources of free radicals:

$$C_6H_5{-}NH{-}N{=}N{-}Alk \rightarrow C_6H_5{-}NH\cdot + N_2 + Alk^{\cdot}. \qquad (6)$$



$$(CH_3)_2\underset{\displaystyle CN}{\underset{|}{C}}{-}N{=}N{-}\underset{\displaystyle CN}{\underset{|}{C}}(CH_3)_2 \rightarrow 2(CH_3)_2\dot{C}(CN) + N_2, \qquad (7)$$

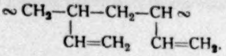
where alk = $CH_3{-}$, $CH_2{=}CH{-}CH_2{-}$, $C_6H_5CH_2{-}$.

As was established previously, these radicals, and likewise the radical $(CH_3)_2\dot{C}(CN)$, differ markedly from each other in their reactivity in abstracting an H-atom from organic compounds [4].

Sulfur monochloride was also used in this work together with the radicals mentioned. It is known that sulfur monochloride is a strong agent for building up. The hypothesis has been put forward in the literature [5] that the vulcanizing action of sulfur monochloride is due to the development of a radical type of reaction. In connection with this, it seemed interesting to study the action of sulfur monochloride in dilute polymer solutions. Natural rubber (NR) containing only units connected in the 1,4-position

$$\sim CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CH_2{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CH_2 \sim, \qquad (8)$$

synthetic polyisoprene (SPI), containing a considerable number (up to 90 %) of units connected at 1,4 and polydivinyl rubber (SRB) with the majority of units connected at 1,2 (up to 70%).



$$\sim CH_2-\underset{\displaystyle CH=CH_2}{CH}-CH_2-\underset{\displaystyle CH=CH_2.}{CH}\sim \qquad (9)$$

were used for the study.

The experimental results from determining the reduced viscosity of benzene solutions of these rubbers when heated with the above compounds, in a nitrogen atmosphere, are given in Table 1. Experiments with azoisobutyric dinitrile (D) were carried out at 80° and those with methylphenyltriazene (M) and S_2Cl_2 at 100°. Heating was continued for 5 hours in the case of S_2Cl_2 and 1-2 hours for the rest. The above differences in experimental conditions were due to the different decomposition kinetics of the initiators.

The data obtained confirm the above hypothesis on the existence of two competing directions of the reaction of free radicals with polymers. All three rubber samples were destroyed when in low concentrations, while with higher concentrations, they formed gels. However, the reaction intensity in both cases depends substantially on the polymer structure and the activity of the free radicals.

First of all, it should be noted that radicals of such low activity as benzyl and allyl, which are incapable of reactions breaking a C−H bond [4], remained ineffective even in breaking a carbon-carbon bond. The more active methyl radical caused gel formation in NR and SPI at concentrations of 2.7-3.0% and above, while at lower concentrations it caused destruction. Gel formation was observed in the case of SRB rubber at a polymer concentration of only 1.0%, as this rubber is characterized by a large number of vinyl groups in the chain. This agrees with the known capacity of side vinyl groups to add free radicals readily [6]. The fact that SRB has little tendency to be destroyed may be due to the insignificant number of diallyl units with weakened carbon-carbon bonds in the polymer chain of this rubber. The radical $(CH_3)_2\dot{C}(CN)$, which has relatively low activity, did not produce gel formation in NR and SPI even at very high polymer concentrations (up to 10%) but invariably caused destruction. This is due to the low capacity of inner double bonds in a polymer chain to add free radicals of low activity. At certain polymer concentrations this radical does produce gel formation with SRB rubber, which contains a large number of side vinyl groups. The high reactivity of outer double bonds (vinyl groups) with $(CH_3)_2\dot{C}(CN)$ had been indirectly established earlier during the investigation of the products of reaction of this radical with olefins [7].

The behavior of sulfur monochloride seemed especially interesting. When a solution of S_2Cl_2 was introduced at room temperature into a rubber solution, regardless of concentration, the solution gelled. However, when the solution was then heated, the gel disappeared and the solution viscosity decreased to the value given in Table 1. Only in certain cases (polyisoprene and SRB) at high concentrations did the gel formed at the beginning of the experiment not disappear.

Besides studying the viscosity of rubber solutions it seemed necessary to determine directly the mean molecular weight of the original rubber and samples subjected to free radical action, as an explanation for the decrease in rubber solution viscosity could perhaps have been found without recourse to the idea of polymer chain destruction, as for example, by considering the formation of rigid globules impervious to the solvent, (due to intramolecular macromolecule vulcanization) and having other hydrodynamic constants. For this purpose two solutions of natural rubber in benzene (NR-I and NR II) were prepared and heated with azoisobutyric dinitryl (D), methylphenyltriazene (M) and sulfur monochloride. The molecular weight M was measured by using an ultracentrifuge. As is known [8]:

$$M=\frac{S_0}{D_0}\cdot\frac{R\cdot T}{1-v\cdot\rho}, \qquad (10)$$

where S_0 and D_0 are sedimentation and diffusion constants, R is the universal gas constant, T the absolute temperature, V, the partial specific volume of the dissolved polymer and ρ, the solvent density. Octane was used as solvent in experiments for determining S_0 and D_0. The rubbers were transferred directly from the benzene solution into octane without precipitation, by the gradual change of the solvent [9]. The sedimentation constant

TABLE 1

Viscosity of Benzene Solutions of Rubbers after Heating with Diazoamino Compounds (2 hours at 100°), Azoisobutyric Dinitrile (1 hour at 80°) and Sulfur Monochloride (5 hours at 100°)

Natural rubber. Reduced viscosity of the original solution $\eta_{red} = 12.05$								Synthetic polyisoprene. Reduced viscosity of the original solution. $\eta_{red} = 5.23$				Synthetic polyisoprene. Reduced viscosity of the original solution. $\eta_{red} = 5.23$				Polydivinyl polymer SRB. Reduced viscosity of the original solution. $\eta_{red} = 4.15$			
$R^{\cdot}$	Rubber conc. wt. %	Initiator conc. (% of rubber)	$\eta_{red.}$	$R^{\cdot}$	Rubber concentration in weight (%)	Initiator conc (% rubber)	$\eta_{red.}$	$R^{\cdot}$	Rubber concentration (in weight, %)	Initiator concentration (in % of rubber)	$\eta_{red.}$	$R^{\cdot}$	Rubber concentration (in wt. %)	Initiator concentration (in % of rubber)	$\eta_{red.}$	R	Rubber concentration (in wt. %)	Initiator Concentration (in % of rubber)	$\eta_{red.}$
$CH_3^{\cdot}$	1.0	5	1.83	$(CH_3)_2\dot{C}(CN)$	1.0	5	1.12	$CH_3^{\cdot}$	0.3	20	0.80	$(CH_3)_2\dot{C}(CN)$	0.3	50	0.76	$CH_3^{\cdot}$	0.3	5	1.72
		10	1.04			20	1.05			100	1.37		1.0	10	2.40		1.0	5	2.95
		20	0.71		3.0	5	1.68		1.0	10	1.12			50	2.41			20	Gel
	2.0	10	2.63			20	1.30			100	1.12		3.0	5	2.82		2.0	1	6.91
		40	1.95		5.0	5	1.46		3.0	5	2.47			10	2.34			5	Gel
		100	2.15			20	1.37			10	2.86			30	2.17		3.0	1	Gel
	2.5	20	2.94		10.0	5	2.56			20	Gel		5.0	3	3.80	$(CH_3)_2\dot{C}(CN)$	1.0	20	3.92
		100	3.12	S_2Cl_2	0.5	5	0.80			100	Gel			5	3.75			50	3.78
	2.6	20	4.70		1	5	0.61		4.0	5	2.69			10	3.83		2.0	50	3.98
	2.7	20	Gel		2	5	0.65			10	Gel	S_2Cl_2	0.5	5	0.62		3.0	20	Gel
	3.0	10	Gel		3.	5	1.31			40	Gel		1	5	0.78		5.0	20	Gel
	5.0	10	Gel		4	5	1.72		5.0	5	4.48		2	5	1.66	S_2Cl_2	0.5	5	3.72
$(CH_3)_2\dot{C}(CN)$	0.3	5	0.59	$C_6H_5\dot{C}H_2$	0.5	5	11.73			10	Gel		3	5	2.25		1.0	5	3.82
		50	0.51	$CH_2{=}CH{-}CH_2^{\cdot}$	0.5	5	12.23			40	Gel		4	5	Gel		2.0	5	Gel

S_0 was calculated by extrapolation to infinite dilution using the equation:

$$\frac{1}{S}=\frac{1}{S_0}+kC, \tag{11}$$

which gives satisfactory results at sufficiently high dilutions [10]. The values of the sedimentation coefficients S were determined by the shift in the maximum in the sedimentation diagram, obtained by Svensson's optical method [11]. With the usual corrections the value S was reduced to 20° and 1 atm. [12].

The diffusion coefficient D was determined for all samples at a starting concentration of 2-2.5 mg/ml, with Lamb's apparatus, fitted with an optical scale, a thermoregulator (± 0.003°) and an automatic device for photographing the scale. For calculating the molecular weight we used the coefficient D_A computed by the method of ordinates and planes as this gives results which correlate better with data for narrow fractions [9]. Concentration effects were excluded by the Boltzman-Gralen method [13] by the asymmetry of the diffusion diagrams. Practically, this procedure was needed only in the case of original rubber samples as deviation from symmetry of the destroyed samples was within the limits of accuracy of the measurement (2-3%). Special control experiments confirmed the adequacy of such a procedure. The value D_A was also reduced to 20°. According to our measurements the ratio $(R\cdot T/1-\bar{V}\cdot\rho)$ was equal to $9.18\cdot 10^{10}$ for isoprene rubber in octane.

TABLE 2

Results of Molecular Weight (M_m) Measurements for Natural Rubber Samples.

Substance	$S_0\cdot 10^{13}$	$(D_A)_0\cdot 10^7$	$M_m\cdot 10^{-3}$	$\langle r^2\rangle^{1/2}$ A
NR-I	9.09	1.65	614	664
NR-I + D (a)	5.71	3.38	155	212
NR-I + D (b)	5.88	4.37	127	267
NR-I + S_2Cl_2	3.85	6.33	56	143
NR-II	14.7	1.07	1263	844
NR-II + D	4.26	5.22	75	173
NR-II + M	4.13	5.66	67	159
NR-II + S_2Cl_2	3.85	6.33	56	143

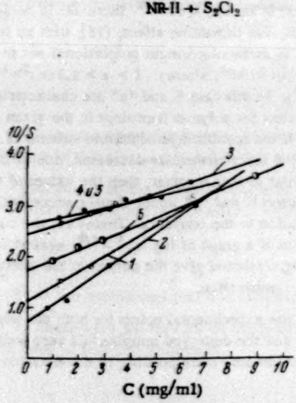


Fig. 1. The relation of sedimentation coefficients to concentration for NR-I and NR-II in octane. 1) NR-I, 2) NR-II, 3) NR-II + M, 4) NR-I + + S_2Cl_2, 5) NR-II + S_2Cl_2, 6) NR-1 + D (a).

The molecular weight calculated by this method using formula (10) was close to the most probable (i.e., corresponding to the maximum of the weight distribution) weight M_m.

Inverse values of the sedimentation coefficients (10/S) as functions of concentration are shown in Fig. 1 for a number of samples. Results of the measurements are given in Table 2. The average error in the determination of S_0 and D_0 was not more than 4-5%.

Thus, there is an indisputable and, furthermore, very strong destruction effect caused by the free radicals. The similarity of the M_m values obtained for all destroyed samples and especially the fact that the same results were obtained for both samples in the case of S_2Cl_2, indicate that the decomposition of the chains was of a random character, with equal probability of breakage in any of the monomer links.

As was shown independently by Durup [14] and Charlesby [15], after the third or fourth break all traces of the original distribution are lost and the resulting molecular-weight distribution approaches a Poisson distribution, with the same parameter values, regardless of the previous history of the sample.

As an independent control, the osmotic pressure π of four samples of the NR-II series was measured at the same concentration (9.1 mg/ml). Benzene with equal portions of dissolved M, D and S_2Cl_2 was used as solvent. As the difference in the levels in osmometry is inversely proportional to M (an average molecular weight is obtained here which is substantially lower than the most probable) then the results given in Table 3 are well correlated with the original data.

TABLE 3

Results of Determination of the Osmotic Pressure of Solutions

Height of column (in mm)	NR-II	NR-II + D	NR-II + M	NR-II + S_2Cl_2
Outer capillary	0.5	9.0	18.0	11.2
Inner capillary	20.0	72.0	78.5	68.0
Difference in level	19.5	63.0	60.5	56.8

Besides this, it was interesting to find out whether intramolecular sewing together in the macromolecules was occurring parallel with the destruction. With this in mind an evaluation of the effective macromolecular dimensions was carried out based on the theory of Kirkwood-Riseman [16] and Mandelkern-Flory [17]. Combination of the basic equations of these theories results in the equation:

$$F = 5.1 \langle r^2 \rangle^{1/2}, \tag{12}$$

where: $F = (M/S_0)(1 - V \cdot \rho) \cdot N$ (N=Avogadro's number) or $R \cdot T/D_0 N$ is the friction coefficient of one macromolecule. Substitution of the appropriate values in (12) gives $< r^2 >^{1/2} = (M/S_0) \cdot 9.83 \cdot 10^{-24}$ cm (see the last column in Table 2) for the mean square of the distance between the ends of the molecule.

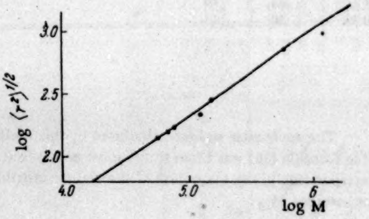


Fig. 2. The relation of the mean square of the distance between the ends of the molecule to molecular weight for the samples NR-II, NR-II + M; NR-II + D, NR-II + S_2Cl_2.

As is known, $< r^2 >^{1/2}$ increases in nonideal solvents, due to volume effects [18], with an increase in molecular weight proportional not to $M^{1/2}$ but to M^a, where: $1 > a > 0.5$ ($< r^2 >^{1/2} = KM^a$). In this case K and "a" are characteristic parameters for polymer homologs in the given solvent. If the specific hydrodynamic volume of the destroyed macromolecules decreased, due to intramolecular sewing together, then the values of the parameters K and "a" would change accordingly (in relation to the original). Therefore, the construction of a graph of log $< r^2 >^{1/2}$ against log M (see Fig. 2) should give the answer to the question under consideration.

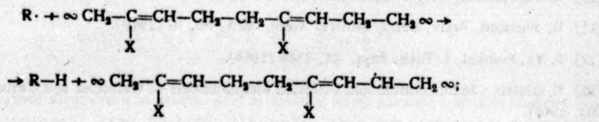
The experimental points for both the original rubber and the destroyed samples fall very well in one straight line corresponding to the equation:

$$\langle r^2 \rangle^{1/2} = K \cdot M^{0.647}. \tag{13}$$

The value of the index "a" (0.620) was very close to that found earlier for synthetic polyisoprene rubber. Thus, the values of the parameters K and "a" do not change during the destruction of natural rubber. This provides a sufficient basis for considering that no intramolecular chain vulcanization occurs during this process.

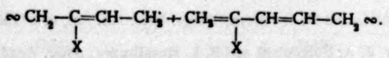
The hypothesis based on Equation (5), of the reaction of free radicals with weakened carbon-carbon bonds, is in accordance with experimental results; however, on the basis of the ideas expressed by N. N. Semenov [1], on the greater probability of scheme [1] rather than scheme [2], the mechanism of this reaction could be considered as proceeding in two stages:

1) abstraction of an H-atom from the polymer chain with the formation of a polymer radical:



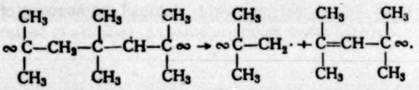
$$R\cdot + \infty CH_2-\underset{X}{\underset{|}{C}}=CH-CH_2-CH_2-\underset{X}{\underset{|}{C}}=CH-CH_2-CH_2\infty \rightarrow$$
$$\rightarrow R-H + \infty CH_2-\underset{X}{\underset{|}{C}}=CH-CH_2-CH_2-\underset{X}{\underset{|}{C}}=CH-\dot{C}H-CH_2\infty; \qquad (14)$$

2) decomposition of the polymer radical to form a diene grouping at the end of the chain and an allyl radical:



$$\infty CH_2-\underset{X}{\underset{|}{C}}=CH-CH_2^{\cdot} + CH_2=\underset{X}{\underset{|}{C}}-CH=CH-CH_2\infty. \qquad (15)$$

Such considerations appear less applicable to polyisobutylene destruction, as in this case the decomposition is accompanied by the formation of a more active primary polymer radical:



$$\infty\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-\dot{C}H-\underset{CH_3}{\overset{CH_3}{C}}\infty \rightarrow \infty\underset{CH_3}{\overset{CH_3}{C}}-CH_2\cdot + \underset{CH_3}{\overset{CH_3}{C}}=CH-\underset{CH_3}{\overset{CH_3}{C}}\infty. \qquad (16)$$

Only on the basis of a detailed investigation of the process on model systems could the problem of the mechanism of the elementary act in this process be solved.

It follows from the results of this work that in the process of polymerization it is necessary to allow for the development of destructive processes in which active centers and polymer radicals take part.

SUMMARY

1. It was established that free radicals produce destruction of polymer chains.

2. Ideas were put forward on the possible mechanism of the reaction leading to the breaking of a carbon-carbon bond in polymer molecules.

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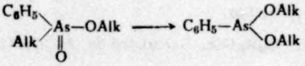
THE INTERACTION OF ALKYL IODIDES WITH SILVER SALTS OF PHENYLALKYLARSINIC ACIDS

Gilm Kamai and I. M. Starshov

Crafts [1] first obtained alkyl esters of arsenic acid by treating silver arsenate with alkyl iodides in a sealed tube heated on a water bath. Later, Michaelis [2] found that silver phenylarsinate reacted with alkyl halides to form phenylarsinic esters. In 1947 Ya. F. Komissarov, A. Ya. Maleeva and A. S. Sorokoumov [3] described a method of obtaining alkylarsinic esters by heating alkyl iodide with silver alkylarsinates suspended in dry benzene or toluene. Using this method, one of us [4] synthesized several alkyl esters of arsenic acid.

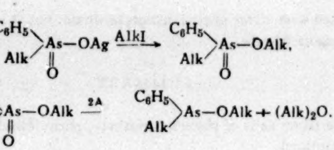
To determine if the thermal conversion of phenylalkylarsinic esters (I) into phenylalkylarsinous esters (II) was possible by using the reaction of Komissarov et al. [3],



$$(C_6H_5)(Alk)As(=O)-OAlk \longrightarrow C_6H_5-As(OAlk)_2$$

(I) (II)

we attempted the synthesis of the former esters by reacting the appropriate silver salts with alkyl iodides. However, we were unable to isolate these esters. Instead of the phenylalkylarsinic esters expected, the phenylalkylarsinous esters were obtained in all cases, probably according to the scheme:



$$(C_6H_5)(Alk)As(=O)-OAg \xrightarrow{AlkI} (C_6H_5)(Alk)As(=O)-OAlk,$$

$$(C_6H_5)(Alk)As(=O)-OAlk \overset{2A}{—} (C_6H_5)(Alk)As-OAlk + (Alk)_2O.$$

An analogous reaction leading to the formation of esters of acids containing trivalent arsenic had been described earlier by Michaelis [2].

EXPERIMENTAL

The starting materials, phenylalkylarsinic oxides, were prepared in the usual way [5].

Preparation of silver phenylmethylarsinate. 70 g of phenylmethylarsinic oxide was oxidized with 200 ml of 5 N nitric acid in a porcelain dish on a water bath. After removal of excess nitric acid by evaporating down several times with water, the phenylmethylarsinic acid was neutralized with aqueous ammonia. Then silver phenylmethylarsinate was obtained by adding an aqueous solution of silver nitrate. The salt was separated off, recrystallized from hot water, sucked dry on a filter funnel, washed with acetone and dried in a desiccator. It was a fluffy white powder which could give strongly supersaturated aqueous solutions.

Found %: Ag 34.89. $C_7H_8O_2AgAs$. Calculated %: Ag 35.16.

The Action of Methyl Iodide on Silver Phenylmethylarsinate

Experiment 1. 42 g of silver phenylmethylarsinate, 50 ml of dry benzene and 17.5 g of methyl iodide were put into a half liter, dark blue bottle with a ground-glass stopper. Then the bottle was shaken at room temperature for 5 hours. Examination of the contents of the bottle showed that esterification did not occur under these conditions. The silver phenylmethylarsinate was recovered almost quantitatively.

Experiment 2. 42 g of silver phenylmethylarsinate, 50 ml of pure benzene and 16 g of methyl iodide were put into a 300 ml round-bottomed flask, fitted with a reflux condenser and a methanical stirrer. The contents of the flask were heated on a water bath and stirred for 2 hours. Then the precipitate was filtered off and washed with dry benzene. The yellow-colored benzene filtrate was distilled. A fraction was isolated with b. p. 89-91° (14 mm), n_D^{20} 1.5740.

Found %: As 38.07, 37.95. $C_8H_{11}OAs$. Calculated %: As 37.82.

The analytical data and the boiling point indicated that the material obtained was the methyl ester of phenylmethylarsinous acid.

Preparation of silver phenylethylarsinate. 37 g of phenylethylarsinic oxide was oxidized with 5 N nitric acid and then was treated first with aqueous ammonia and finally with aqueous silver nitrate solution to give silver phenylethylarsinate as a fluffy white powder which was readily soluble in hot water.

Found %: Ag 33.24. $C_8H_{10}O_2AgAs$. Calculated %: Ag 33.62.

The action of ethyl iodide on silver phenylethylarsinate. 20 g of silver phenylethylarsinate, 15 g of ethyl iodide and 50 ml of dry benzene were heated in a flask with a reflux condenser on a water bath and stirred for 3 hours. On distilling the benzene filtrate, a high-boiling fraction was isolated with b. p. 88-89° (7 mm).

d_0^0 1.2091, d_0^{20} 1.1912, n_D^{20} 1.5520.

Found %: As 33.18, 33.21. $C_{10}H_{15}OAs$. Calculated %: As 33.14.

The material isolated was the ethyl ester of phenylethylarsinous acid.

Preparation of silver phenyl-n-butylarsinate. 27 g of phenyl-n-butylarsinate was oxidized with 5 N nitric acid and treated as above to give silver phenyl-n-butylarsinate as a fluffy, white powder. The salt was difficultly soluble in acetone and cold water.

Found %: Ag 30.54. $C_{10}H_{14}O_2AgAs$. Calculated %: Ag 30.91.

Butyl bromide was treated with silver phenyl-n-butylarsinate, but it was not possible to isolate a single reaction product from the benzene filtrate.

SUMMARY

1. For the first time, the silver salts of phenyl-, methyl-, phenylethyl- and phenyl-n-butylarsinic acids have been synthesized and examined.

2. It was established that in the reaction of silver phenylalkylarsinates with alkyl iodides (in benzene with heating) only the corresponding alkyl esters of phenylalkylarsinous acids are formed.

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DIARYLBROMONIUM AND DIARYLCHLORONIUM SALTS

A. N. Nesmeyanov, N. V. Kruglova, R. B. Mamerikova and T. P. Tolstaya

It was shown experimentally by one of us and L. G. Makarova [1] that, as expected, the diazo decomposition of aryldiazonium fluoborates occurs heterolytically with the transfer of the phenyl residue as a positively charged fragment which attacks the molecules of the medium electrophylically. Thus, a meta-substituted diphenyl is formed preponderantly by the decomposition of phenyldiazonium fluoborate in nitrobenzene and in phenyltrimethylammonium salts. It is known that homolytic decomposition of phenyldiazo compounds gives principally o- and p-nitrodiphenyl with nitrobenzene. Two of the authors of this article obtained for the first time diphenylbromonium and diphenylchloronium cations and a number of corresponding salts [2] by the diazo decomposition of phenyldiazonium fluoborates in bromobenzene and chlorobenzene media; thus the phenyl cation produced by the diazonium fluoborate adds to the free electron pair of the halobenzene chlorine or bromine, forming a diphenylhalonium cation. The passivity of the free electron pairs of chlorine and bromine in halobenzenes was illustrated by the very small yield of onium compounds. Besides, a second possible reason for this is the low temperature stability (in relation to diazonium fluoborates) of diphenylbromonium and diphenylchloronium salts.

In the present article we describe the use of the same method of obtaining bromonium and chloronium compounds for the synthesis of a number of unsymmetrical diarylhalonium salts with substituents in the benzene nucleus. The majority were obtained by decomposition of various aryldiazonium fluoborates in bromobenzene and chlorobenzene. Another halobenzene was used in only one case, and here p-dichlorobenzene decomposed phenyldiazonium fluoborate to produce phenyl-p-chlorophenylchloronium salts. The properties of the diarylbromonium and diarylchloronium salts that we obtained in this work are similar to the properties we described earlier for diphenylbromonium and diphenylchloronium salts. Diarylbromonium iodides are slightly soluble in water and decompose when stored for approximately 24 hours or at a temperature between 60-80°. The bromides are soluble and are more stable to temperature. The salts of complex anions are much more stable, especially chloroplatinates (which decompose in a range close to 150°) and tetraphenylborate salts. Diarylchloronium salts with complex anions are noticeably less stable than the corresponding bromonium ones. Diarylchloronium halides are completely unstable. Diarylhaloniums are typical salts, insoluble in nonpolar solvents, many of them are soluble in water, alcohol and nitromethane. They exchange anions in solution with the usual rapidity of ionic reactions.

EXPERIMENTAL

Phenyl-p-tolylbromonium salts. 59 g (0.29 moles) of p-tolyldiazonium fluoborate was added in small portions over 6 hours to 100 ml (0.94 mole) of bromobenzene, heated to 70-78° (thermometer in liquid) and stirred vigorously. Heating was continued for a further 1.5 hours until no more BF_3 was evolved and after this the reaction mixture was cooled to room temperature, when a dark oil separated from the bromobenzene layer and collected in the bottom of the flask. Both parts of the reaction mixture were treated many times with water (10-15 ml). The treatment was discontinued when a drop of the water extract no longer gave a precipitate with aqueous sodium iodide. Spot tests with β-naphthol showed that diazo material was present in only the 1st and 2nd extracts.

The aqueous extracts, containing phenyl-p-tolylbromonium fluoborate, were extracted with ether and used for preparing phenyl-p-tolylbromonium salts with various anions. Solutions of phenyl-p-tolylbromonium fluoborate in water were stable when stored frozen in solid carbon dioxide. The yield of phenyl-p-tolylbromonium fluoborate was found to be 0.75% of the theoretical by precipitation of aliquot portions of the solutions with sodium iodide.

Phenyl-p-tolylbromonium fluoborate (0.03 g) was isolated by freezing the 2nd aqueous extract from the oil. On reprecipitation with ether from methyl alcohol it had decomp. point 78° and appeared as colorless crystals which were readily soluble in acetone and alcohol, slightly less in water and insoluble in ether.

Found %: C 46.40, 46.19; H 3.87, 3.89. $C_{13}H_{12}BrF_4B$. Calculated %: C 46.60; H 3.61.

Phenyl-p-tolylbromonium iodide. A few drops of concentrated sodium iodide solution were added to 20 ml of the aqueous extract. The white precipitate was immediately filtered off, washed with water and reprecipitated from methyl alcohol with ether. Its weight was 0.08 g. The salt was readily soluble in acetone, alcohols and nitromethane, difficultly in cold water, insoluble in ether and hydrocarbons and was decomposed by boiling water. Decomp. point 81-82°. At room temperature it became yellow in 1-2 minutes, smelled of iodobenzene and bromobenzene and became moist. It could be stored in solid carbon dioxide for about 24 hours.

Found %: C 41.62, 41.72; H 3.19, 3.10; Br 21.09, 21.04. I 33.64.. $C_{13}H_{12}BrI$. Calculated %: C 41.62; H 3.23; Br 21.30; I 33.83.

Double dalt of phenyl-p-tolylbromonium iodide and mercuric iodide. 1-2 ml of alcohol was added to 20 ml of aqueous extract followed by an aqueous solution of HgI_2 in NaI until precipitation was complete. The fine, lemon-yellow, needle-like crystals were filtered off, washed with water, alcohol and ether and reprecipitated from nitromethane with ether. The weight of the precipitate was 0.13 g. The salt was appreciably soluble in alcohol, readily soluble in nitromethane, insoluble in ether and was decomposed by acetone. The decomposition point was 110-111°. The salt was stable at room temperature for 1-2 days.

Found %: C 18.65, 18.61; H 1.47, 1.41; Br 9.33, 9.29. $C_{13}H_{12}BrI_3Hg$. Calculated %: C 18.81; H 1.46; Br 9.63.

Phenyl-p-tolylbromonium tetraphenylborate. An equal volume of alcohol was added to 15 ml of aqueous extract and then a concentrated aqueous solution of $(C_6H_5)_4BNa$ until precipitation was complete. The flocculent precipitate was filtered off, washed with water, alcohol and ether and twice reprecipitated from acetone with ether. The material formed soft, white needles with decomp. point 135° (changes at 117°), which were very readily soluble in acetone, almost insoluble in alcohol and water and insoluble in ether and hydrocarbons. The salt could be stored at room temperature for a few hours. It was completely stable on storing in solid carbon dioxide.

Found %: C 77.98, 77.87; H 5.69; 5.69; Br 14.03, 14.18, 14.19; B 1.83, 2.13. $C_{37}H_{32}BrB$. Calculated %: C 78.31; H 5.69; Br 14.09; B 1.91.

Phenyl-p-tolylbromonium chloroplatinate. Yellow-pink phenyl-p-tolylbromonium chloroplatinate was precipitated from 15 ml of aqueous extract with a solution of platinic chloride in 10% hydrochloric acid. The precipitate was washed with water, alcohol and ether. The weight was 0.3 g. The salt was reprecipitated from nitromethane with ether. It could be recrystallized from nitromethane. Decomp. point 152°. The salt was readily soluble in nitromethane, slightly soluble in acetone, almost insoluble in alcohol and insoluble in ether and benzene. It was completely stable at room temperature.

Found %: C 34.35, 34.30; H 2.66, 2.52; Hal 41.04; Pt 21.48, 21.67. $C_{26}H_{24}Cl_6Br_2Pt$. Calculated %: C 34.54; H 2.67; Hal 41.20; Pt 21.53.

Treatment of very cold aqueous extract with solid sodium bromide gave phenyl-p-tolylbromonium bromide, which was readily soluble in water, alcohol and acetone and insoluble in ether. Decomp. point 109-110°.

Anion exchange reactions in phenyl-p-tolylbromonium salts. 0.007 g of solid phenyl-p-tolylbromonium fluoborate was dissolved in the minimum amount of water. Sodium bromide was added in portions to the cooled solution until precipitation was complete. The bromide obtained (shiny, light, flaky crystals) was filtered off and carefully washed with two drops of ice water, one drop of cold alcohol and absolute ether. Decomp. point 109°. The bromide was dissolved in water. Crystalline sodium iodide was added to the solution. The precipitated iodide was filtered off, washed with water and reprecipitated from alcohol with ether. Decomp. point 78-80°.

The iodide was added in portions to a suspension of mercuric iodide in nitromethane until the mercuric iodide dissolved. The solvent was evaporated to give a precipitate of yellow crystals with decomp. point 108-110°.

Phenyl-o-tolylbromonium salts. 44.7 g (0.22 mole) of o-tolyldiazonium fluoborate was decomposed in 100 ml (0.94 moles) of bromobenzene at 60-65° under the conditions described above. The reaction was accompanied by vigorous evolution of BF_3 and was quickly complete. The experiment was treated analogously to that described above. The yield of bromonium fluoborate was 0.6%.

Phenyl-o-tolylbromonium fluoborate (0.32 g) was isolated by freezing 30 ml of aqueous extract. After reprecipitation from alcohol with ether, the salt was shiny, colorless crystals with decomp. point 112-113°. It was readily soluble in alcohol and acetone, less soluble in nitromethane and insoluble in ether. The dry salt was stable,but in water slowly decomposed (even in the cold).

Found %: C 46.47, 46.41; H 3.78, 3.97. $C_{13}H_{12}BrF_4B$. Calculated %: C 46.60; H 3.61.

Phenyl-o-tolylbromonium iodide. Treatment of 10 ml of phenyl-o-tolylbromonium fluoborate solution with concentrated sodium iodide solution gave 0.12 g of an iodide as a fine light cream powder with decomp. point 65-66°. The salt was completely insoluble in water, alcohol, acetone, ether and benzene. It slowly dissolved in nitromethane but with decomposition. It could be stored in solid carbon dioxide for 1-2 days.

The double salt of phenyl-o-tolylbromonium iodide and mercuric iodide (0.02 g) was prepared by adding a few drops of a concentrated solution of HgI_2 in NaI to 1 ml of fluoborate solution. The salt was a finely crystalline precipitate with decomp. point 92°, which was insoluble in water, alcohol and ether and was decomposed by acetone and nitromethane. The salt was stable for a few days when stored in solid carbon dioxide.

Phenyl-o-tolylbromonium chloroplatinate. Treatment of 7 ml of fluoborate solution with a solution of platinic chloride in 10% hydrochloric acid, gave 0.1 g of bromonium chloroplatinate with decomp. point 142°. The salt was a fine pink powder which was very slightly soluble in nitromethane. It was stable at room temperature.

Phenyl-o-tolylbromonium bromide was prepared by treating a saturated, aqueous solution of bromonium fluoborate with solid sodium bromide and was shiny white crystals with decomp. point 83°.

Phenyl-2,4-xylylbromonium salts. 30 g (0.146 mole) of 2,4-xylyldiazonium derivative was decomposed in 50 ml of bromobenzene at 60-65°. The reaction product was worked up as in the previous experiments.

Phenyl-2,4-xylylbromonium fluoborate. By long and strong cooling of the aqueous extract, about 0.015 g of bromonium fluoborate was isolated. On being reprecipitated twice from alcohol with ether, the salt formed long white needles with decomp. point 103.5-104.5°, which were soluble in acetone, alcohol and water and insoluble in ether and benzene.

Found %: C 48.00; H 4.14. $C_{14}H_{14}BrF_4B$. Calculated %: C 48.18; H 4.04.

Phenyl-2,4-xylylbromonium iodide was precipitated from 15 ml of aqueous extract at 0° with solid NaI. The precipitate was washed with water, cold (−10°) alcohol and ether. Its weight was 0.24 g. After reprecipitation from a mixture of nitromethane and alcohol (1:1) with ether (at −5°), 0.07 g of white crystals were isolated with decomp. point 66°, which were difficultly soluble in alcohol, nitromethane, dioxane and acetone.

Found %: C 43.13, 42.97; H 3.63, 3.65; Hal 53.21. $C_{14}H_{14}BrI$. Calculated %: C 43.19; H 3.63; Hal. 53.16.

Double salt of phenyl-2,4-xylylbromonium iodide and mercuric iodide. It was difficultly soluble in alcohol and decomposed in acetone; decomp. point 100°.

Found %: C 19.84, 19.58; H 1.89, 2.13. $C_{14}H_{14}BrI_3Hg$. Calculated %: C 19.93; H 1.67.

Phenyl-β-naphthylbromonium salts. 30 g (0.136 mole) of β-naphthyldiazonium derivative was decomposed in 100 ml of bromobenzene at 95-100°. The decomposition went very sluggishly. A large amount of tarry material was left in the flask and was filtered off at the end of the experiment. Further treatment was as described above.

Phenyl-β-naphthylbromonium iodide. 70 ml of aqueous extract was treated with solid sodium iodide to give 0.01 g of material in the form of grey needles. After two reprecipitations from nitromethane with ether, it had decomp. point 77°.

Found %: C 46.57; H 3.29. $C_{16}H_{12}BrI$. Calculated %: C 46.74; H 2.94.

Phenyl-p-chlorophenylbromonium salts. 40 g (0.18 mole) of p-chlorophenyldiazonium fluoborate was decomposed in 100 ml (0.94 mole) of bromobenzene at 92-97° under the conditions already described. The experiment was worked up as previously.

Phenyl-p-chlorophenylbromonium chloroplatinate. The bromonium chloroplatinate was precipitated from 15 ml of aqueous extract with a solution of platinic chloride in 10% hydrochloric acid. After two reprecipitations from nitromethane with ether, 0.02 g of salt were obtained with decomp. point 137-138°. The salt was appreciably soluble in water, alcohol and acetone, readily soluble in nitromethane and insoluble in ether and benzene; it was stable at room temperature.

Found %: C 30.48, 30.25; H 1.89, 1.89; Hal 46.55; Pt 20.74. $C_{24}H_{18}Cl_8Br_2Pt$. Calculated %: C 30.50; H 1.92; Hal 46.94; Pt 20.65.

Double salt of phenyl-p-chlorophenylbromonium iodide and mercuric iodide. A solution of Na_2HgI_4 was added to 20 ml of aqueous extract. The precipitate was reprecipitated three times from nitromethane with ether. The salt crystallized as short, sand-colored needles with decomp. point 97-98°. It was readily soluble in nitromethane, moderately soluble in alcohol, appreciably soluble in water and was decomposed by acetone. The pure salt was stable at room temperature for 12 hours. All purification processes should be carried out at a temperature not higher than 1-5°.

Found %: C 17.18, 17.21; H 1.13, 1.02. $C_{12}H_9ClBrI_3Hg$. Calculated %: C 16.95; H 1.06.

Phenyl-p-carbethoxyphenylbromonium salts. 41 g (0.145 moles) of p-carbethoxyphenyldiazonium fluoborate was decomposed in 100 ml (0.94 mole) of bromobenzene at 70-75°. Further treatment was as described above.

Phenyl-p-carbethoxyphenylbromonium iodide. Saturated NaI solution at 0° was added to 15 ml of aqueous extract to give 0.05 g (0.5%) of the bromonium iodide. The yellow crystals, with decomp. point 53-54°, were quite unstable; at 14-16° they completely decomposed in 8-10 hours, at −30 to −35°, in 25-30 days; the salt was insoluble in alcohol and ether; it dissolved with decomposition in acetone, nitromethane and dioxane.

Found %: C 41.28, 41.14; H 3.23, 3.31; Hal 48.19. $C_{15}H_{14}O_2BrI$. Calculated %: C 41.61; H 3.26; Hal 47.75.

Phenyl-p-carbethoxyphenylbromonium tetraphenylborate. 3 ml of aqueous sodium tetraphenylborate solution was added to 10 ml of aqueous extract to give 0.03 g (0.25%) of the tetraphenylborate salt. It was twice reprecipitated from acetone with ether. The shiny, white flakes had decomp. point 142-144° (at 110-112° they turned yellow).

Found %: C 74.89, 74.48; H 5.60, 5.72; Br 13.04; B 1.73. $C_{39}H_{34}O_2BrB$. Calculated %: C 74.87; H 5.49; Br 12.74; B 1.73.

Phenyl-p-carbethoxyphenylbromonium chloroplatinate. A few drops of concentrated chloroplatinic acid were added to 25 ml of aqueous extract at 0°. The precipitate was filtered off, washed quickly with cold (−5°) alcohol and ether and reprecipitated twice from nitromethane with ether. The yield was 0.08 g. The salt appeared as shiny orange plates with decomp. point 127° (at 90-94° it darkened); it was soluble in acetone and nitromethane, difficultly soluble in water, decomposed by alcohol and insoluble in ether; it was stable.

Found %: C 35.12, 35.15; H 2.88, 2.84. $C_{30}H_{28}O_4Cl_6Br_2Pt$. Calculated %: C 35.30; H 2.76.

The double salt of phenyl-p-carbethoxyphenylbromonium iodide and mercuric iodide was precipitated from 20 ml of aqueous extract by adding concentrated Na_2HgI_4 solution. The yield was 0.09 g (0.2%). After two reprecipitations from nitromethane with ether, the salt appeared as long yellow needles with decomp. point 79°, stable in the solid state, difficultly soluble in alcohol, insoluble in water and ether and soluble in acetone with decomposition.

Found %: C 27.35, 27.35; H 2.23, 2.33; Hal 50.83, 50.27. $C_{30}H_{28}O_4Br_2I_4Hg$. Calculated %: C 27.38; H 2.14; Hal 50.54.

Phenyl-p-tolylchloronium salts. 57 g (0.28 moles) of p-tolyldiazonium fluoborate was decomposed in 100 ml (0.98 mole) of chlorobenzene at 70-78°. The procedure and the working up process for the synthesis of diarylchloronium salts were the same as those described at the beginning of the experimental section for diarylbromonium salts. The yield of phenyl-p-tolylchloronium fluoborate was 1.86%.

Double salt of phenyl-p-tolylchloronium iodide and mercuric iodide. A solution of Na_2HgI_4 was added to 10 ml of aqueous extract to give 0.3 g of canary yellow, fine,needle-like crystals with decomp. point 93-94°. The salt was appreciably soluble in alcohol, readily soluble in acetone and nitromethane and insoluble in ether. It was stable at room temperature for several days.

Found %: C 19.92, 20.13; H 1.62, 1.63; Cl 4.61, 4.81. $C_{13}H_{12}ClI_3Hg$. Calculated %: C 19.87; H 1.54; Cl 4.51.

Phenyl-p-tolylchloronium tetraphenylborate. 0.18 g of phenyl-p-tolylchloronium tetraphenylborate with decomp. point 127° (changed at 115°) was prepared from 10 ml of aqueous extract by similar methods to those described above for the corresponding bromonium salt.

The salt crystallized as soft white needles. It was readily soluble in acetone, almost insoluble in alcohol and insoluble in ether. It could be stored at room temperature for several days.

Found %: C 84.77, 84.64; H 6.18, 6.22; Cl 6.71, 6.95; B 2.15, 2.16. $C_{37}H_{32}ClB$. Calculated %: C 85.00; H 6.17; Cl 6.78; B 2.07.

Phenyl-p-tolylchloronium chloroplatinate. 0.02 g of phenyl-p-tolylchloronium chloroplatinate was precipitated from 8 ml of aqueous extract with chloroplatinic acid. After reprecipitation from nitromethane with ether, the salt had decomp. point 139°. It was completely stable at room temperature.

Found %: C 38.52; H 3.09; Pt 23.51. $C_{26}H_{24}Cl_6Pt$. Calculated %: C 38.30; H 2.97; Pt 23.93.

Phenyl-o-tolylchloronium salts. 17 g (0.082 moles) of o-tolyldiazonium fluoborate was decomposed in 100 ml (0.98 mole) of chlorobenzene at 57-62°. The experiment was worked up as described above. The yield of fluoborate was 0.63%.

Double salt of phenyl-o-tolylchloronium iodide and mercuric iodide. 3 ml of fluoborate solution gave 0.08 g of the salt as a fine, canary-colored precipitate, which was very quickly decomposed. After two reprecipitations from nitromethane with ether, the salt had decomp. point 64°. The isolation and purification had to be carried out at a low temperature. The salt could be stored for several days in solid carbon dioxide.

Phenyl-o-tolylchloronium chloroplatinate was an almost insoluble light pink powder with decomp. point 123-124°. The double salt of phenyl-2,4-xylylchloronium iodide and mercuric iodide was prepared and purified as described in the case of the analogous diarylbromonium salt. Form light yellow needles with decomp. point 83°.

Found %: C 21.14, 21.35; H 1.76, 1.82. $C_{14}H_{14}ClI_3Hg$. Calculated %: C 21.04; H 1.76.

Phenyl-p-chlorophenylchloronium salts. A. Decomposition of p-chlorophenyldiazonium fluoborate in chlorobenzene. 40 g (0.18 mole) of p-chlorophenyldiazonium fluoborate was decomposed in 100 ml (0.98 mole) of chlorobenzene at 95-98°. The experiment was worked up as described above. The yield of product was 0.21%.

B. Decomposition of phenyldiazonium fluoborate in p-dichlorobenzene. 30 g (0.16 mole) of phenyldiazonium fluoborate was decomposed in 80 g (0.54 mole) of molten p-dichlorobenzene at 57-60°. The experiment was worked up as described above. The yield of product was 0.5%.

Phenyl-p-chlorophenylchloronium chloroplatinate. Chloroplatinic acid was added to 10 ml of aqueous extract, obtained in Experiment A. The pale pink precipitate was filtered off and washed with water, alcohol and ether. Its weight was 0.12 g. The salt was appreciably soluble in water, alcohol and acetone, insoluble in ether and readily soluble in nitromethane (however, with partial decomposition). After reprecipitation with ether from nitromethane, it had decomp. point 119-120°.

Found %: C 33.24; H 2.00. $C_{24}H_{18}Cl_{10}Pt$. Calculated %: C 33.66; H 2.12.

Double salt of phenyl-p-chlorophenylchloronium iodide and mercuric iodide. A cold Na_2HgI_4 solution was added to 15 ml of aqueous extract obtained in Experiment A. Immediately a very fine, light yellow precipitate came out, which quickly darkened and became flocculent and was filtered off and washed with water and ether. After two reprecipitations from nitromethane with ether, the salt was obtained as fine, brownish yellow needles with decomp. point 84°. It was soluble in alcohol, readily soluble in nitromethane and insoluble in ether. It was decomposed by acetone. The salt was purified at 1-5° and was stored in solid carbon dioxide. An identical salt was prepared from Experiment B.

Found %: C 17.71, 17.66; H 1.10, 1.10; $C_{12}H_9Cl_2I_3Hg$. Calculated %: C 17.89; H 1.13.

Phenyl-p-carbethoxyphenylchloronium salts. The decomposition of 40 g (0.145 mole) of p-carbethoxyphenylchloronium fluoborate in 100 ml (0.98 mole) of chlorobenzene, was carried out at 70-75°. The experiment was worked up as described above.

Phenyl-p-carbethoxyphenylchloronium tetraphenylborate was prepared similarly to the corresponding bromonium salt. 20 ml of aqueous extract gave 0.1 g (0.34%) of material with decomp. point 121-124° (it turned pink at 108-110°). The salt was stable, soluble in acetone and nitromethane and difficultly soluble in alcohol and water.

Found %: C 80.53, 80.23; H 5.98, 5.97; Cl 6.21, 6.40; B 1.92, 1.72. $C_{39}H_{34}O_2ClB$. Calculated %: C 80.61; H 5.91; Cl 6.10; B 1.86.

Phenyl-p-carbethoxyphenylchloronium chloroplatinate. Treatment of 30 ml of aqueous extract with chloroplatinic acid at 0° gave 0.07 g of chloronium chloroplatinate, which, after two reprecipitations from nitromethane with ether, appeared as shiny orange plates with decomp. point 106.5-108°. The salt was soluble in acetone and difficultly soluble in water and dilute alcohol; it was stable.

Found %: C 38.92, 38.78; H 3.04, 3.04; Cl 29.56; Pt 20.61. $C_{30}H_{28}O_4Cl_8Pt$. Calculated %: C 38.68; H 3.03; Cl 30.46; Pt 20.96.

The double salt of phenyl-p-carbethoxyphenylchloronium iodide and mercuric iodide (0.05 g, 0.2%) was prepared from 10 ml of aqueous extract by adding Na_2HgI_4 solution at 0°. After two reprecipitations from nitromethane with ether (at −10°), the salt * appeared as long, thin, yellow needles with decomp. point 58.6-60°, which were unstable under normal conditions. At 20-25°, the material decomposed completely in 24 hours with the separation of HgI_2. The salt was difficultly soluble in alcohol, insoluble in water and soluble in acetone with decomposition.

Found %: C 29.46, 29.48; H 2.42, 2.43. $C_{30}H_{28}O_4Cl_2I_4Hg$. Calculated %: C 29.25; H 2.29.

SUMMARY

For the first time a number of unsymmetrical diarylbromonium and diarylchloronium salts, containing various substituents in one of the benzene nuclei, were obtained by the decomposition of various aryldiazonium fluoborates in bromobenzene, chlorobenzene and p-dichlorobenzene, and their properties are described.

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* The freshly precipitated impure product was very unstable and with an insignificant rise in the temperature, above −3-0°, it was immediately converted into an oil and red HgI_2 separated.

CATALYTIC SYNTHESIS OF N-BUTYLAMINE ON MIXED OXIDE CATALYSTS

F. V. Belchev and N. I. Shuikin

Investigation of the amination of aliphatic alcohols besides its practical value due to the increased application of amines in various branches of the national economy, is also valuable for understanding the nature of the chemical reaction between alcohols and ammonia on highly developed catalyst surfaces. In the literature there are many papers devoted to the study of the conditions of the conversion of alcohols into amines on individual catalysts, in a pure form or deposited on the surfaces of porous bodies.

Sabatye and Meil [1] studied the reactions of alcohols with ammonia in the presence of a number of individual catalysts and showed that amines of the aliphatic series are obtained in greatest yields in the presence of aluminum oxide at 350-380°. Briner and Gandillon [2] found the optimal conditions of methyl alcohol amination were in the presence of aluminum oxide at 405°. Dornell [3] and E. and K. Smolenskie [4] obtained a relatively high yield of ethylamine also in the presence of aluminum oxide at 340-350° and a molar ratio of ammonia and ethanol equal to 1:2. Popov [5] established that platinized silica gel was an active catalyst for aminating alcohols.

Thus, for example, n-butyl alcohol gave a catalyzate with a 68% amine content in the presence of platinized silica gel at 450° and a molar ratio of ammonia and alcohol of 4.9:1.

There are a few papers in the literature on the investigation of the amination of alcohols over mixed catalysts, and they mention the higher activity of mixed catalysts as compared with individual ones. In the investigation of the reaction of the simplest aliphatic alcohols with ammonia in the presence of various catalysts, Brown and Reid [6] established that mixed catalysts (silica gel with thorium oxide and silica gel with nickel oxide) were more effective than pure aluminum oxide. One of us [7] investigated the relative performance of mixed catalysts composed of aluminum oxide and oxides of iron, chromium, tin and zinc in the dehydration of ethyl alcohol and ammonia. A comparison of the performance of these catalysts showed that the most active of them was a mixture of 90 % Al_2O_3 and 10 % Fe_2O_3. In comparison with pure aluminum oxide, this mixed catalyst decomposed ethyl alcohol less by 2-3 times at 360-400° and gave ethylamines in the same or slightly greater yield. A. A. Balandin and V. E. Vasserberg established [8] that catalysts containing several phases have a higher activity than single phase catalysts as the most active sections of the surface are situated at the phase boundaries. Not only mixtures of different materials, but also homogeneous bodies capable of undergoing polymorphous conversions at definite temperatures may be used as such multiphase catalysts. This suggests that the most suitable catalysts for alcohol amination would be multiphase ones with high dehydration and adsorption capacities.

In this investigation we examined the comparative effect of catalysts composed of mixtures of aluminum oxide with oxides of iron and titanium in different weight ratios, on n-butyl alcohol amination at different temperatures and flow rates of ammonia and alcohol vapor through the catalyst. With this in mind, investigated the activity of the following catalysts: pure aluminum oxide, Al_2O_3 (95%) + Fe_2O_3 (5 %), Al_2O_3 (85%) + + Fe_2O_3 (15%), Al_2O_3 (95%) + TiO_2 (5%), Al_2O_3 (85%) + TiO_2 (15%). The experimental data obtained showed that a mixture of aluminum oxide (85%) and ferric oxide (15%) was the most effective of the catalysts examined. In the presence of this catalyst at 405° and under the other conditions adopted by us, the catalyzate contained 42.8% of mixed butylamines. The catalyzate obtained under the same amination conditions with pure aluminum oxide contained 37.2% of mixed butylamines.

EXPERIMENTAL

The mixed catalysts Al_2O_3 (95%) + Fe_2O_3 (5%) and Al_2O_3 (85%) + Fe_2O_3 (15%) were prepared by adding ammonium hydroxide to mixed solutions of aluminum and iron nitrates to precipitate aluminum and iron hydroxides. The hydroxide precipitates were washed with water and centrifuged to remove NO_3^- and, after drying off, they were moulded in a press. The moulded catalysts were dried at 120°.

The catalysts Al_2O_3 (95%) + TiO_2 (5%) and Al_2O_3 (85%) + TiO_2 (15%) were prepared by precipitating aluminum hydroxide from aluminum nitrate solution with ammonium hydroxide and adding separately prepared titanium hydroxide to the precipitate with vigorous stirring. The washed and centrifuged precipitate of combined aluminum and titanium hydroxides, was moulded and dried at 120°. Before use, a slow stream of ammonia was passed through each catalyst at 450° for 1 hour.

The starting n-butyl alcohol boiled at 116-117° (756 mm) on redistillation and had d_4^{20} 0.8106 and n_D^{20} 1.3991.

The experiments were carried out in the usual apparatus of the circulating type [7]. Ammonia from an evaporating reservoir was passed through a drying column with caustic potash and calcium chloride into a heated silica flask, where it was mixed with alcohol vapor. The ammonia-alcohol mixture was then passed into a silica tube, heated with an electric furnace and filled with catalyst (a layer 40 cm long). The exit end of the catalyst tube was connected to a catalyzate collector, placed in a cooling mixture. The collector was connected through a reflux condenser and a wash bottle, with dilute sulfuric acid, to a graduated gas holder. The temperature of the electric furnace was controlled with a nichrome-constantan thermocouple. The rate of flow of ammonia and alcohol vapor through the catalyst was determined by a rheometer. Each experiment was continued for 1 hour. A molar ratio of ammonia to n-butyl alcohol of 4 : 1 was chosen.

The catalyzates obtained in all the experiments were two-layer liquids; the upper layer was pale green or yellowish-brown and had a strong ammoniacal smell. The catalyzate was first treated with solid caustic potash, then the upper layer was separated from the lower (water), weighed and analyzed for amine nitrogen content by Francois' method [9]. The unsaturated hydrocarbon, hydrogen and saturated hydrocarbon content of the gaseous products was determined.

In all the cases where a complete analysis of the catalyzate had to be carried out, the amines were extracted from it by three treatments with dilute hydrochloric acid (1: 1) and water. Nonamines were distilled off from the acid extract and the amines were isolated by caustic potash treatment, after which they were carefully distilled. The results of catalytic amination of n-butyl alcohol at volume rates of 0.6, 0.75 and 0.9 are given in Tables 1 and 2. The consumption of alcohol at these volume rates was 40.6, 45.7 and 54.3 g, respectively.

Comparison of the experimental data obtained, showed that in comparison to pure aluminum oxide, the mixture of aluminum (85%) and iron (15%) oxides had the greatest activity of the catalysts used. This catalyst increased the speed of n-butyl alcohol amination, in comparison with pure aluminum oxide, by an average of 30%, and lowered the alcohol decomposition rate by a factor of 2; at the same time its catalytic activity decreased more slowly. The yields of catalyzate in the presence of the alumino-iron catalyst were higher than the yields obtained with pure aluminum oxide under the same conditions, by 1.5-2 times. This increase in the yields is largely explained by the fact that n-butyl alcohol was dehydrated into butylene in the presence of Al_2O_3 at 390-420° at a greater rate than in the presence of the alumino-iron catalyst. Besides this, the experimental data showed that in the presence of this mixed catalyst, the decomposition of butylamines was reduced. In connection with this, the amine nitrogen content of the catalyzates, obtained over Al_2O_3 + 15% Fe_2O_3, reached 3.3-3.8% and 1.7-2.2% calculated on the n-butyl alcohol used, which exceed the corresponding values, obtained in experiments with pure aluminum oxide under the same conditions, by 25-30%. The gaseous products, obtained on amination of n-butyl alcohol in the presence of this catalyst at 375-420°, contained 20-25% of unsaturated hydrocarbons, 65-70% of hydrogen and a small quantity of paraffins; in contact with pure aluminum oxide under the same conditions, 85-90% of unsaturateds, 2.5-4% of hydrogen and also a small quantity of paraffins were formed. Thus the optimal conditions for the amination of n-butyl alcohol were a temperature

TABLE 1

Catalytic Amination of n-Butyl Alcohol

Temperature of experiment	Volume rate	Amount of catalyzate (g)	Amount of gas separated (liters)	Amount of amine nitrogen in catalyzate (%)	Volume rate	Amount of catalyzate (g)	Amount of gas separated (liters)	Amount of amine nitrogen in catalyzate (%)	Volume rate	Amount of catalyzate (g)	Amount of gas separated (liters)	Amount of amine nitrogen in catalyzate (%)
Pure Al_2O_3												
375°	0.6	17.6	4.9	2.25	0.75	20.0	4.7	2.35	0.9	22.0	6.8	2.24
390	0.6	15.6	6.95	3.23	0.75	17.5	6.5	3.78	0.9	13.2	10.2	4.42
405	0.6	12.8	11.4	3.88	0.75	17.0	8.0	4.08	0.9	12.4	11.0	4.87
420	0.6	7.5	12.6	4.8	0.75	9.7	10.2	4.84	0.9	8.7	12.0	6.12
Al_2O_3 (95%) + Fe_2O_3 (5%)												
375	0.6	25.3	6.5	1.92	0.75	27.5	6.5	1.33	0.9	28.4	8.5	2.45
390	0.6	26.6	6.8	2.36	0.75	28.5	6.0	1.66	0.9	22.8	9.2	3.02
405	0.6	27.6	8.5	2.25	0.75	28.0	7.0	1.47	0.9	18.5	9.4	3.45
420	0.6	14.4	9.8	3.03	0.75	15.6	10.0	1.04	0.9	16.5	11.8	3.7
Al_2O_3 (85%) + Fe_2O_3 (15%)												
375	0.6	26.0	8.0	2.09	0.75	26.6	8.0	3.95	0.9	28.0	9.05	3.15
390	0.6	21.4	8.4	3.36	0.75	28.0	9.5	3.47	0.9	32.0	9.08	3.05
405	0.6	20.0	9.4	3.35	0.75	27.0	9.8	3.84	0.9	31.0	11.5	3.26
420	0.6	16.2	10.2	3.06	0.75	20.0	11.4	3.40	0.9	20.0	11.9	3.85
Al_2O_3 (95%) + TiO_2 (5%)												
375	0.6	25.3	6.0	1.99	0.75	23.0	4.5	3.05	0.9	34.2	6.4	2.27
390	0.6	18.4	7.0	3.16	0.75	22.0	6.8	3.35	0.9	27.2	8.0	2.67
405	0.6	17.5	10.6	3.38	0.75	20.8	7.5	3.60	0.9	25.0	8.3	2.90
420	0.6	10.4	11.7	4.36	0.75	9.6	12.0	6.8	0.9	14.5	10.2	5.87
Al_2O_3 (85%) + TiO_2 (15%)												
375	0.6	21.0	6.8	2.17	0.75	20.8	8.4	2.65	0.9	29.0	6.2	2.62
390	0.6	18.6	7.9	2.96	0.75	20.2	9.6	2.78	0.9	29.0	6.2	2.80
405	0.6	17.3	8.2	3.60	0.75	19.3	9.8	3.82	0.9	25.0	8.1	2.82
420	0.6	6.5	10.8	6.27	0.75	4.8	12.3	6.68	0.0	8.6	9.9	4.15

of 390° and a volume rate of 0.75 at a molar ratio of ammonia and alcohol of 4 : 1. Under these conditions the yield of amines reached 25%, calculated on the original alcohol. To determine the composition of the material formed in the amination of n-butyl alcohol in the presence of this catalyst, we took 104 g of combined catalyzate containing 3.84% of amine nitrogen; 38.24 g of amines and 56.53 g of nonamines were isolated from this. The amine portion was distilled at 754 mm and the following fractions were isolated:

1st 45.77°, 0.76 g; 2nd 77-78°, 16.80 g, d_4^{20} 0.7462, n_D^{20} 1.3952; 3rd 78-159°, 2.47 g; 4th 159-160°, 4.30 g; d_4^{20} 0.7546, n_D^{20} 1.4063; 5th 160-215°, 1.05 g; 6th 215-217°, 4.07 g, d_4^{20} 0.7690, n_D^{20} 1.4242; residue 1.95 g.

According to properties, the 2nd fraction was n-butylamine [10], the 4th, di-n-butylamine [11] and the 6th, tri-n-butylamine [12]. The nonamines were fractionated at 768 mm under the same conditions. The following fractions were obtained:

1st 45-75°, 0.5 g; 2nd 75-76°, 1.27 g, d_4^{20} 0.8102, n_D^{20} 1.3821; 3rd 76-86°, 0.7 g; 4th 86-116°, 2.3 g; 5th 116-117°, 43.3 g, d_4^{20} 0.8104, n_D^{20} 1.3991; residue 5.4 g.

The 2nd fraction consisted largely of butyraldehyde and the 5th fraction of unchanged n-butyl alcohol. Besides these substances, analysis showed that nitriles [13] were present in the catalyzate as 3.5-4.7%.

TABLE 2

The Composition of the Amines, Formed in Catalytic Amination of n-Butyl Alcohol

Temperature of experiment	Volume rate	Composition of amines (in%)			Total amines in catalyzate (%)	Volume rate	Composition of amines (%)			Total amines in catalyzate (%)	Volume rate	Composition of amines (%)			Total amines in catalyzate (%)
		Primary	Secondary	Tertiary			Primary	Secondary	Tertiary			Primary	Secondary	Tertiary	
Pure Al_2O_3															
390°	0.6	17.6	6.6	5.3	29.5	0.75	20.8	12.2	4.4	32.4	0.9	19.8	10.6	9.8	40.2
405	0.6	16.4	10.5	7.2	34.1	0.75	18.4	8.5	10.3	37.2	—	—	—	—	—
Al_2O_3 (95%) + Fe_2O_3 (5%)															
390	0.6	13.8	4.9	2.9	21.6	0.75	10.6	8.5	5.4	24.5	—	—	—	—	—
405	0.6	3.9	15.2	1.2	20.3	0.75	12.4	6.3	3.6	22.3	0.9	17.5	12.4	6.5	36.1
Al_2O_3 (85%) + Fe_2O_3 (15%)															
390	0.6	15.2	18.4	4.8	38.4	0.75	16.7	7.5	15.4	39.6	0.9	15.0	3.9	16.0	34.9
405	0.6	16.4	14.3	6.9	37.6	0.75	17.5	20.5	4.8	42.8	—	—	—	—	—
Al_2O_3 (95%) + TiO_2 (5%)															
390	0.6	14.4	12.8	4.4	31.2	0.75	18.2	4.7	9.6	32.5	0.9	6.3	8.4	6.2	20.9
405	—	—	—	—	—	0.75	10.5	10.7	12.2	33.4	—	—	—	—	—
Al_2O_3 (85%) + TiO_2 (15%)															
390	0.6	9.3	10.5	12.3	32.1	0.75	13.6	6.2	4.5	24.3	0.9	12.0	7.7	6.8	24.5
405	—	—	—	—	—	—	11.4	8.6	8.2	28.2	—	—	—	—	—

The catalyst consisting of 95% Al_2O_3 and 5% Fe_2O_3 had an activity between that of pure aluminum oxide and the mixed catalyst 85% Al_2O_3 and 15% Fe_2O_3. The alumino-titanium catalysts were less active than the mixed catalysts of aluminum and iron oxides. Nevertheless, the catalyst of 95% Al_2O_3 and 5% TiO_2 had a higher activity than pure aluminum oxide. However, during the reaction, the alumino-titanium catalyst gradually became covered with a black deposit of "coke" and after 2-3 hours of continuous operation, its activity rapidly decreased. The amine nitrogen content of catalyzates, obtained with an alumino-titanium catalyst, reached 5.8% in separate experiments; however, they have a high capacity for dehydrating alcohol to form an unsaturated hydrocarbon. A certain advantage of alumino-titanium catalysts over pure aluminum oxide is the possibility of carrying out the amination of n-butyl alcohol over them at a lower temperature. Pure aluminum oxide, with the ammonia-alcohol mixture flowing over it at a volume rate of 0.6, shows the greatest activity at 405°. Then the amine nitrogen content of the catalyzate reaches 4.87%.

SUMMARY

1. The reaction between n-butyl alcohol and ammonia was investigated in the presence of pure aluminum oxide and mixed catalysts, composed of aluminum oxide and ferric and titanium oxides at temperatures of 375-420°, a molar ratio of ammonia to alcohol of 4 : 1 and volume rates of 0.6, 0.75 and 0.9.

2. A mixed catalyst composed of 85% Al_2O_3 and 15% Fe_2O_3 was the most active in comparison with pure aluminum oxide.

3. The alumino-titanium catalyst, although more active than pure aluminum oxide, loses its activity comparatively quickly.

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CONCLUSIONS

1. [illegible]

2. [illegible]

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THE REACTION BETWEEN HEXACHLOROETHANE AND ISOPROPYL ALCOHOL INITIATED BY BENZOYL PEROXIDE

G. A. Razuvaev, B. N. Moryganov and A. G. Kronman

We have published several papers [1] on reactions of carbon tetrachloride with alcohols, initiated by peroxides. These reactions are interesting examples of chain reactions in the liquid phase. We decided to expand these investigations to include other halide derivatives. It was shown that perchloroethylene was formed by the reaction of hexachloroethane with methyl alcohol in sealed tubes at 200-220° [2]:

$$CCl_3{-}CCl_3 + CH_3OH \rightarrow CCl_2{=}CCl_2 + 2HCl + CH_2O.$$

The reaction between hexachloroethane and ethyl alcohol [3] proceeded similarly.

In this work we decided to investigate the reaction of hexachloroethane with isopropyl alcohol, initiated by benzoyl peroxide. Isopropyl alcohol was chosen as it was used as an example in our detailed investigation of the chain reactions of carbon tetrachloride with alcohols.

Experiments conducted with different benzoyl peroxide concentrations showed that the reaction occurs at the boiling point of the mixture (1 mole isopropyl alcohol and 0.125 mole hexachloroethane with the separation of HCl and formation of acetone, perchloroethylene and, probably, pentachloroethane. Furthermore, the decomposition products of the peroxide, CO_2, benzene and benzoic and phthalic acids, were detected.

In this reaction, as well as in the case of reaction of carbon tetrachloride with alcohols, the process has a chain mechanism. The products obtained, for example HCl and acetone, show that this is the case. If 24.1 moles of HCl and 16.7 moles of acetone are obtained for each mole of peroxide decomposed during the thermal decomposition of 0.0124 mole of benzoyl peroxide in the same amounts of isopropyl alcohol (1 mole) and hexachloroethane (0.125 mole), then under the same conditions 73.3 moles of HCl and 37 moles of acetone are obtained for each mole of decomposed peroxide during the decomposition of 0.0021 mole of peroxide with the same amount of components. The course of the process may be followed very conveniently by the amount of HCl separated. The chain reaction may also be determined by the acetone yield, but the drawbacks of this type of investigation are the possibility of secondary reactions and the difficulty of determining the amount of acetone produced. Therefore, in further experiments we determined the extent of the process only by determining the quantities of HCl. The process may be illustrated by the following scheme.

Initiation:

$$(C_6H_5COO)_2 \rightarrow 2C_6H_5COO\cdot; \tag{1}$$

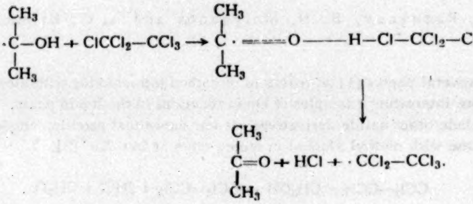
$$C_6H_5COO\cdot \rightarrow C_6H_5\cdot + CO_2. \tag{2}$$

Chain beginning:

$$C_6H_5COO\cdot + CH_3CHOHCH_3 \rightarrow C_6H_5COOH + CH_3\dot{C}OHCH_3; \qquad (3)$$

$$C_6H_5\cdot + CH_3CHOHCH_3 \rightarrow C_6H_6 + CH_3\dot{C}OHCH_3. \qquad (4)$$

The chain:



$$\cdot\overset{CH_3}{\underset{CH_3}{C}}-OH + ClCCl_2-CCl_3 \rightarrow \overset{CH_3}{\underset{CH_3}{C}}\cdot ===O——H-Cl-CCl_2-CCl_3; \qquad (5)$$

$$\downarrow$$

$$\overset{CH_3}{\underset{CH_3}{C}}=O + HCl + \cdot CCl_2-CCl_3. \qquad (6)$$

Chain transmission:

$$CCl_3-CCl_2\cdot \rightarrow CCl_2=CCl_2 + Cl\cdot; \qquad (7)$$

$$CCl_3-CCl_2\cdot + CH_3CHOHCH_3 \rightarrow CH_3\dot{C}OHCH_3 + CCl_3-CCl_2H; \qquad (8)$$

$$Cl\cdot + CH_3CHOHCH_3 \rightarrow CH_3\dot{C}OHCH_3 + HCl \text{ etc} \qquad (9)$$

Break of chain:

$$2CH_3\dot{C}OHCH_3 \rightarrow CH_3COCH_3 + CH_3CHOHCH_3. \qquad (10)$$

We had considered earlier that the intermediate product formed was

$$CH_3-C(OH)Cl-CH_3.$$

On the basis of V. V. Voevodsky's hypothesis, we now accept the formation of an energetically more probable intermediate complex as in (5). The formation of the pentachloroethyl radical has been accepted earlier in papers on the free-radical chlorination of saturated hydrocarbons by hexachloroethane [4] and also the photodecomposition of pentachloroethane [5]. The pentachloroethyl radical readily decomposes with the formation of perchloroethylene and chlorine, which continues the chain. However, we separated a fraction from the reaction products mixture which was very close to the one corresponding to pentachloroethane. Thus, it is possible that besides pentachloroethyl-radical decomposition, a hydrogen is abstracted by it from alcohol with the formation of pentachloroethane (8). It should be noted that the radicals abstract hydrogen from alcohol with greater facility than from hydrocarbons and this may explain the absence of pentachloroethane in products of hydrocarbon chlorination [4].

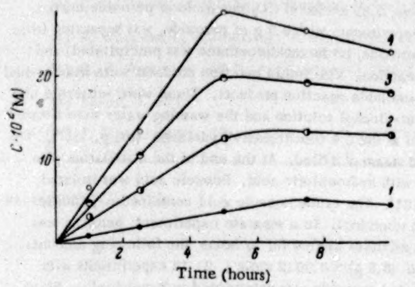


Fig. 1. The relation of the quantity of HCl separated to time.
Concentration of peroxide: $2.4 \cdot 10^{-3}$ M (1), $1.2 \cdot 10^{-2}$ M (2), $2.4 \cdot 10^{-2}$ M (3), $3.6 \cdot 10^{-2}$ M (4).

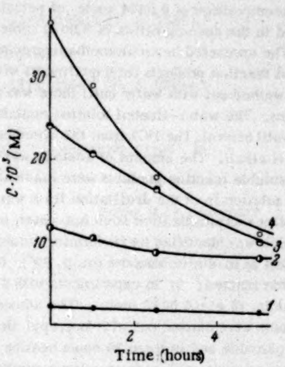


Fig. 2. The relation of benzoyl peroxide decomposition to time.
Peroxide concentrations (1-4) the same as in Fig. 1.

For a fuller investigation of the process, we carried out several experiments to determine the chain length of the reaction investigated at 70°, and some kinetic curves were plotted.

The relation of the quantity of HCl separated for different peroxide concentrations to time is shown in Fig. 1. It can be seen from the curves that the quantity of HCl increases rapidly at the beginning of the reaction and then a small decrease is noticeable, apparently due to secondary reactions. Figure 2 shows the relation of benzoyl peroxide decomposition to time. On the basis of the decrease in peroxide concentration and increase in separated HCl in the first hour of the reaction, an approximate chain length was estimated for different peroxide concentrations according to the formula

$$v = \frac{\Delta C_{HCl}}{\Delta t} : \frac{\Delta C_{b.p.}}{\Delta t},$$

where ν is the length of the chain; $\frac{\Delta C_{HCl}}{\Delta t}$ is the difference in the concentration of HCl separated during a certain time interval; $\frac{\Delta C_{b.p.}}{\Delta t}$ is the difference in benzoyl peroxide concentrations during the same time interval.

It has been established that the length of the chain increases with a decrease in peroxide concentration. Thus, the length of the chain is equal to 7 for a peroxide concentration of $3.6 \cdot 10^{-2}$ mole/liter of the reaction mixture and the length of the chain equals 18 for a peroxide concentration $1.2 \cdot 10^{-2}$ mole/liter of the mixture.

The authors express their thanks to V. A. Shushunov for taking part in the consideration of results.

EXPERIMENTAL

Chain reaction of hexachloroethane with isopropyl alcohol, initiated by benzoyl peroxide. Preliminary experiments were carried out to select the most favorable ratios of the components, as a result of which we kept to a ratio of 1 mole of isopropyl alcohol to 0.125 moles of hexachloroethane. A flask with a ground glass reflux condenser connected to absorbers for HCl and CO_2, was charged with 60 g of isopropyl alcohol, 29.6 g of hexachloroethane and 3 or 0.5 g of benzoyl peroxide, and the mixture was heated on a water bath for 20 hours. In each experiment, half the peroxide was introduced with component charge and the second half after 10 hours heating. The HCl formed was absorbed in distilled water and the CO_2 in saturated barium hydroxide solution. In the decomposition of 0.0124 mole of peroxide, 0.44 mole of CO_2 was evolved per mole of peroxide decomposed and in the decomposition of 0.0021 mole of peroxide, 0.69 mole of CO_2 per mole of peroxide decomposed. The unreacted hexachloroethane precipitated in experiments with 0.5 g of peroxide, was separated from the liquid reaction products (in experiments with 3 g of peroxide, no hexachloroethane was precipitated) and the HCl washed out with water until there was a neutral reaction. The liquid reaction products were also washed with water. The water-alcohol solution contained water-insoluble reaction products. These were separated and washed until neutral. The HCl from the absorbers, the water-alcohol solution and the washing water were titrated with 0.1 N alkali. The amount of acetone was determined as the 2,4-dinitrophenylhydrazone (m. p. 125°). The water-insoluble reaction products were made alkaline and steam-distilled. At the end of the distillation, the alkaline solution from the distillation flask was acidified with hydrochloric acid. Benzoic acid was isolated, which, after recrystallization from hot water, melted at 121°. The crude benzoic acid contained o-phthalic acid, which was identified by its forming fluorescein with resorcinol. In a separate experiment, benzene was determined as m-dinitrobenzene (m. p. 89°). In reaction mixtures heated for 20 hours, the following amounts of peroxide reacted: 1) in experiments with 0.0021 mole (0.5 g) – 0.0012 mole ; 2) in experiments with 0.0124 mole (3 g) – 0.0052 mole . The amount of unreacted peroxide was determined iodometrically. Blank experiments were carried out with isopropyl alcohol (1 mole) and hexachloroethane (0.125 mole) without benzoyl peroxide and in these 20 hours heating yielded: HCl 0.017 g and CH_3COCH_3 0.02 g. The mixture of reaction products (487 g) from a large number of experiments with 20 hour heating,(the amount of components given above and 0.5 g of peroxide) was washed with water until neutral, dried with $CaCl_2$ and then P_2O_5 and distilled on a column. The following were isolated from the distillation:

1. Perchloroethylene, b. p. 120-121°, n_D^{20} 1.5030, d^{20} 1.598, MR_D 30.63; Calc. 30.43. Literature data [6]: b. p. 121°, n_D^{20} 1.50547; d^{20} 1.619.

Found %: Cl 85.02. M 167 (cryoscopic). C_2Cl_4. Calculated %: Cl 85.56. M 166.

2. Pentachloroethane, b. p. 161-163°, n_D^{20} 1.5023, d_4^{25} 1.664, MR_D 35.82; Calc. 35.78. Literature data [7]: b. p. 162°, n_D^{15} 1.50542, d^{15} 1.68813.

Found %: Cl 88.47. M 202.9 (cryoscopic) C_2HCl_5. Calculated %: Cl 87.65. M 202.5.

Kinetics of the hexachloroethane – isopropyl alcohol chain reaction, initiated by benzoyl peroxide. Ampules of about 50 ml capacity were charged with reaction mixture consisting of 30 g (0.5 mole) of isopropyl alcohol , 7.4 g (0.031 mole) of hexachloroethane and different amounts of benzoyl peroxide (0.001, 0.0001, 0.0005 and 0.0015 mole) for different series of experiments. The ampules were sealed off and placed in a thermostat, the temperature of which was maintained at 70 ± 0.1°. After determined time intervals, ampules were removed, quickly cooled and their contents analyzed for HCl produced and unreacted peroxide.

SUMMARY

1. The reaction of hexachloroethane with isopropyl alcohol, initiated by benzoyl peroxide, was investigated. The following reaction products were found: CO_2, HCl, acetone, benzene, benzoic acid, phthalic acid, perchloroethylene and, probably, pentachloroethane.

2. A chain mechanism was proved for the reaction, and a scheme suggested for the process.

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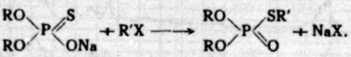
THE REACTIVITY OF ALKALI SALTS OF ACID ALKYLTHIOPHOSPHINIC ESTERS

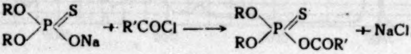
ALKYLATION AND ACYLATION

M. I. Kabachnik, T. A. Mastryukova, N. I. Kurochkin,
N. P. Rodionova and E. M. Popov

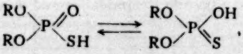
Some time ago we showed [1] that S-alkylated derivatives are formed by alkylation of alkali salts of dialkylthiophosphoric acids with alkyl halides:



Acylation by acyl halides, gave on the contrary, O-derivatives [2]:

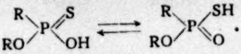


At the same time in another paper [3] the position of the tautomeric equilibrium was determined for free dialkylthiophosphoric acids:



and their methylation with diazomethane was also studied. It seems that the position of the equilibrium depends essentially on the nature of the solvent. Thus, in an alcohol solution the isomer concentration is equal to 1:4 while in a water medium the ratio is reversed to 4:1. Methylation with diazomethane in ether solution gives a mixture of isomers containing 80% of thiol isomer.

Examination of the acid esters of alkylthiophosphinic acids [4] showed that, despite their great similarity, they differed substantially from dialkylthiophosphates in the position of their tautomeric equilibrium: in all the media investigated it was displaced toward the thione form.



A relatively greater yield of thiol methylation derivative was obtained by reaction with diazomethane.

In connection with this, it seemed interesting to study also the reactions of the salts, as had been done for dialkylthiophosphoric acid.

Salts of acid alkylthiophosphinic esters are not described in the literature. The preparation of these salts in a pure form was not simple although the salts of dialkylthiophosphoric acids are very readily available and can be obtained by several convenient methods [1]. The saponification of alkylthionphosphoric esters with alkalies or alcoholates gave only difficultly purifiable products. Better results were obtained from these products by separating the free acids, subsequently purifying them by vacuum distillation and then neutralizing in an alcohol medium. By this method, sodium salts of acid methyl-, ethyl-, propyl- and butylthiophosphinic ethyl esters were obtained.

The infrared spectra of these salts were examined. The spectra of the crystalline salts are shown in Fig. 1. As can readily be seen, the absorption line, characteristic of the P = O bond and lying in the range of 1220 cm^{-1} is absent from the spectra and this indicates a thione structure for the salts [4]. Consequently, the sodium salts of acid alkylthiophosphinic esters do not differ structurally from the corresponding salts of dialkylthiophosphinic acid.

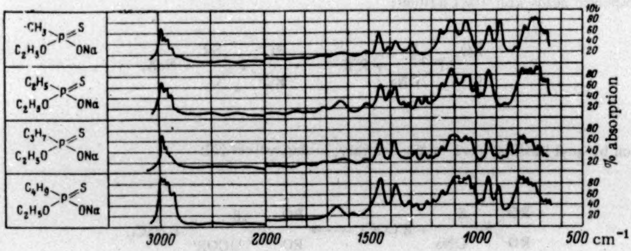
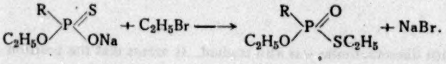


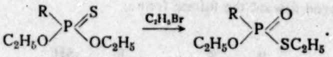
Fig. 1. Infrared spectra of crystalline salts.

We studied the alkylation and acylation of these salts. Alkylation of sodium salts of methyl-, ethyl-, propyl- and butylthiophosphinic ethyl esters with ethyl bromide formed in all cases alkylthiolphosphinic diethyl esters:



$$\mathrm{R(C_2H_5O)P(=S)ONa + C_2H_5Br \longrightarrow R(C_2H_5O)P(=O)SC_2H_5 + NaBr.}$$

We had obtained these esters earlier by a different method [5] – by the isomerization of alkylthionphosphinic esters, by Pishchimuka's method [6]:



$$\mathrm{R(C_2H_5O)P(=S)OC_2H_5 \xrightarrow{C_2H_5Br} R(C_2H_5O)P(=O)SC_2H_5.}$$

The constants of the materials obtained by the alkylation of the salts and isomerization, by Pishchimuka's method, coincided. At the same time, as can be seen from the table (Nos. 1-4), they differed sharply from the constants of the corresponding thione esters.

No. of product	Formula	Preparation method	Boiling point	Pressure (mm)	n_D^{20}	d_4^{20}
1	$CH_3PO(SC_2H_5)(OC_2H_5)$	I*	87—88	(7)	1.4768	1.0951
		II**	106—108.5	(18)	1.4718	1.0904
	$CH_3PS(OC_2H_5)_2$		76.5—78	(13)	1.4610	1.0553
2	$C_2H_5PO(SC_2H_5)(OC_2H_5)$	I	93.5—94.5	(7)	1.4729	1.0658
		II	66.5—68	(2.5)	1.4747	1.0670
	$C_2H_5PS(OC_2H_5)_2$		80—83	(10)	1.4576	1.0324
3	$C_3H_7PO(SC_2H_5)(OC_2H_5)$	I	100—101.5	(8)	1.4721	1.0447
		II	85—86.5	(3)	1.4733	1.0447
	$C_3H_7PS(OC_2H_5)_2$		63.5—65.5	2	1.4596	1.0158
4	$C_4H_9PO(SC_2H_5)(OC_2H_5)$	I	82.5—84	(1)	1.4730	1.0268
		II	98.5—100	(2.5)	1.4728	1.0262
	$C_4H_9PS(OC_2H_5)_2$		74.5—77.5	(2.5)	1.4600	1.0004
5	$CH_3PO(SCH_2OCH_3)(OC_2H_5)$		117.5—120	(2)	1.4778	1.1538
6	$C_2H_5PS(OCOCH_3)(OC_2H_5)$		68—69	(1.5)	1.4701	1.1232

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* Obtained by alkylation.

** Obtained by isomerization.

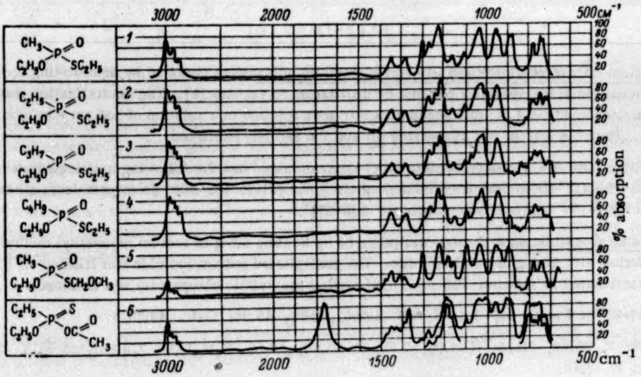
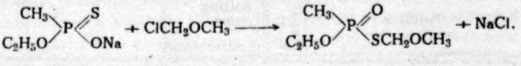


Fig. 2. Infrared spectra of alkylation products.
The numbers of the curves correspond to the numbers in the table.

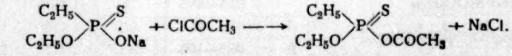
Infrared spectra were also determined for the alkylation products (Fig. 2, 1-4). All of them contained an intense absorption line with a maximum near 1220 cm^{-1}, which is characteristic of the $P=O$ bond, and this confirmed the thiol structure of the esters obtained.

The following thiol derivative was formed by treating sodium ethyl methylthiophosphinate with chloromethyl ether:

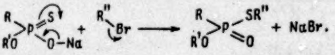


Its structure was proved by the spectrum (Fig. 2, 5). It is interesting to note that chloromethyl ether reacted, in this case, similarly to alkyl halides, while at the same time there are known examples where it reacts as an acylating agent [7].

The acylation of sodium ethyl ethylthiophosphinate with acetyl chloride gave an acetyl derivative which, according to infrared spectra data, has a thione structure:



Thus, in all cases the salts of acid alkylthiophosphinic esters behaved in a way quite similar to the salts of dialkylthiophosphoric acids investigated earlier. Having a thione structure, these salts are alkylated by alkyl halides in an alcohol medium on the sulfur, i.e., with a transfer of reaction center:



However, acylation proceeds on the oxygen with the formation of a derivative whose structure coincides with that of the original salt.

EXPERIMENTAL

The sodium salts of ethyl esters of alkylthiophosphinic acids were prepared by neutralizing the acid esters of alkylthiophosphinic acids, specially purified by distillation in vacuum [4]. The neutralization was carried out with an equimolecular amount of 10% aqueous caustic soda solution or a solution of sodium ethylate in anhydrous ethyl alcohol. Then the solvent was evaporated off and the salt recrystallized.

The sodium salts of alkylthiophosphinic ethyl esters obtained had the following melting points: methylthiophosphinic 216-218° (from petroleum ether), ethylthiophosphinic 185-186° (from petroleum ether), propylthiophosphinic 197-199° and butylthiophosphinic 169-171°.

Methylthiolphosphinic diethyl ester was prepared by heating 6.4 g of sodium monoethyl methylthiophosphinate in alcohol solution with 11.5 g of ethyl bromide. The precipitated sodium bromide was filtered off and the filtrate was fractionated in vacuum. 3.9 g (59%) of diethyl methylthiolphosphinate was obtained:

b. p. 87-88° at 7 mm, n_D^{20} 1.4768, d_4^{20} 1.0951, MR$_D$ 43.36; Calc. 43.35.*

Found %: C 35.40, 35.29; H 7.90, 7.85; P 17.89, 17.96. $C_5H_{13}O_2PS$. Calculated %: C 35.70; H 7.78; P 18.42.

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* In calculating the molecular refraction, the value 8.84 was taken for thiol sulfur and 9.70 for thione sulfur [5, 8].

Ethylthiolphosphinic diethyl ester. The sodium salt was prepared from 5.8 g of sodium ethyl ethylthiolphosphinate and 2.5 g of sodium ethylate in 25 ml of dry ethyl alcohol. 13 g of ethyl bromide was added to the solution obtained and the mixture was heated on a water bath for 3 hours. After filtration and distillation in vacuum, 6.1 g (89%) of diethyl ethylthiolphosphinate was obtained:

b. p. 93.5-94.5° at 7 mm, n_D^{20} 1.4729, d_4^{20} 1.0658, MR_D 47.96; Calc. 47.97.

Found %: C 39.31, 39.41; H 8.53, 8.42; P 16.73, 16.66. $C_6H_{15}O_2PS$. Calculated %: C 39.56; H 8.24; P 17.03.

Diethyl propylthiolphosphinate was prepared by heating 6.0 g of sodium ethyl propylthiolphosphinate in alcohol solution with 10 g of ethyl bromide for 3 hours. 4.6 g (74%) of diethyl propylthiolphosphinate was obtained:

b. p. 100-101.5° at 8 mm, n_D^{20} 1.4721, d_4^{20} 1.0447, MR_D 52.61; Calc. 52.59.

Found %: P 15.21, 15.37. $C_7H_{17}O_2PS$. Calculated %: P 15.77.

Diethyl butylthiolphosphinate was prepared as described above from 5.4 g of sodium ethyl butylthiolphosphinate in 25 ml of ethyl alcohol and 9.5 g of ethyl bromide. The yield was 4.5 g (81%).

B. p. 82.5-84° at 1 mm, n_D^{20} 1.4730, d_4^{20} 1.0268, MR_D 57.45; Calc. 57.21.

Found %: C 45.67, 45.61; H 9.19, 9.16; P 14.41, 14.52. $C_8H_{19}O_2PS$. Calculated %: C 45.67; H 9.10; P 14.73.

O-Ethyl-S-methoxymethyl methylthiolphosphinate. 10 g of chloromethyl ether was added with stirring to 5 g of sodium ethyl methylthiophosphinate in 25 ml of dry ether. The mixture evolved heat and the solution boiled. The reaction mixture was heated on a water bath for 3 hours. The salt precipitate was filtered off and the filtrate distilled in vacuum. 20 g (40%) of O-ethyl-S-methoxymethyl methylthiolphosphinate was obtained:

b. p. 117.5-120° at 2 mm, n_D^{20} 1.4778, d_4^{20} 1.1538, MR_D 45.18; Calc. 45.00.

Found %: P 16.51, 16.60. $C_5H_{13}O_3PS$. Calculated %: P 16.81.

Acetylation of sodium ethyl ethylthionphosphinate with acetyl chloride. 5.5 g of acetyl chloride was added dropwise with stirring to 6.0 g of sodium ethyl ethylthiophosphinate, suspended in 25 ml of dry ether. The mixture heated up slightly and the external appearance of the precipitate changed. The reaction mixture was heated on a water bath so that the ether boiled for 3 hours. Then the salt precipitate was filtered off and the filtrate was fractionated in vacuum. 5.1 g (76%) of the acetyl derivative was obtained:

b. p. 68-69° at 1.5 mm, n_D^{20} 1.4701, d_4^{20} 1.1232, MR_D 48.74; Calc. 48.27.

Found %: C 36.40, 36.40; H 6.62, 6.71; P 15.91, 15.73. $C_6H_{13}O_3PS$. Calculated %: C 36.73; H 6.67; P 15.79.

The infrared spectra were determined on a single-beam Perkin-Elmer 12B spectrometer with automatic photorecording and using NaCl and LiF prisms. The alkylation and acetylation products of the alkali salts of acid alkylthiophosphinic esters were placed between two sylvite plates; the thickness of the layer was identical in all cases and equalled about 0.01 mm. The sodium salts were prepared as suspensions in vaseline oil. The pastes obtained were formed into thin layers between KCl plates. For measurements in the C−H bond absorption region, CCl_4 solutions of the materials were evaporated on sylvite plates. The thicknesses of layers, prepared in this way, were not determined.

SUMMARY

1. The alkylation of sodium salts of alkylthiophosphinic esters was investigated. It was shown that it proceeded with transfer of reaction center and formation of S-alkylated derivatives.

2. The acylation of these same salts was investigated. It was established that it produced O-derivatives.

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* T. p. = C. B. Translation pagination.

SOME RULES IN THE SERIES OF PHOSPHORUS-CONTAINING ACIDS

A. Razumov and Sim-Do-Khen

Two problems aroused our interest during the investigation of various derivatives of alkylphosphinous and dialkylphosphinic acids: 1) the genetic relation between the above compounds and the inorganic acids corresponding to them and 2) the relation of the dissociation constants of phosphorus-containing acids to their structures.

In connection with the first problem, Plets [1] and Kosolapoff [2] consider dialkylphosphinic acids as phosphoric acid derivatives, which have the hydroxyl groups substituted by radicals. Developing this idea in his papers, Plets maintains that dialkylphosphinic acids are in no way related to hypophosphorous acid. He based his views of this problem on two considerations: firstly, on the fact that hypophosphorous acid has no acid chloride, while dialkylphosphinic acids do, and secondly, on the inherent reducing capacity of hypophosphorous acid and the absence of this with dialkylphosphinic acids. We find it rather difficult to agree with this opinion, and, probably, it would be more correct to consider dialkylphosphinic acids as derivatives of hypophosphorous rather than of phosphoric acids.

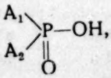
As regards Plets' reasons, it seems best to note first that such a situation is observed also in acids of the aliphatic series. Formic acid does not form an acid chloride and is a reducing agent while its higher homologs possess neither of these properties. However, this is no reason for considering the latter as carbonic acid derivatives. Furthermore, if some of the organic phosphorus compounds are arranged according to their oxidation state, then their genetic relation to the corresponding inorganic compounds becomes even clearer (Table 1).

On examining the data in Table 1, it can be seen that compounds with the same oxidation state are obtained by esterification and isomerization. Compounds with a higher oxidation state are obtained by adding oxygen and halogen (as well as sulfur and selenium) as these reactions are oxidative.

Thus, although dialkylphosphinic acids and hypophosphorous acid have many dissimilarities, they are compounds, nevertheless, of the same oxidation state.

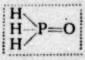
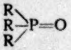
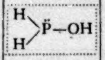
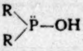
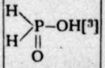
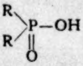
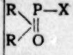
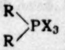
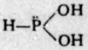
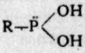
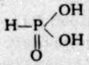
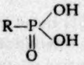
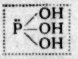
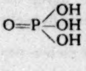
As dialkylphosphinic acids do not have labile hydrogen, it is impossible to expect them to have reducing properties. The problem of why hypophosphorous acids do not form acid chlorides will be discussed further on.

Various types of inorganic acids and organic acids corresponding to them, are given in Table 1.

In examining those which can be expressed by the general formula  where A_1 and A_2 = H, OH, Ar, OR, the regularity of the relation between dissociation constants and the inductive effect (Table 2) is striking.

As can be seen, the acid dissociation constants decrease with decrease of the negative inductive effect of the substituents (A_1 and A_2). The arrangement of the substituents with respect to inductive effect essentially corresponds to data available in the literature, although in some cases there are discrepancies [4, 5].

TABLE 1

Oxidation state	Formal valency	Inorganic compound	Structure of inorganic compound	Organic acids	Acid halide oxide	Acid halides	Esters
2	−1	H_3PO*			—	R_3PX_2	—
					—	$R_2\ddot{P}{-}X$	$R_2\ddot{P}{-}OR$
3	+1	H_3PO_2					$R_2{-}\underset{\underset{O}{\parallel}}{P}(OR)$
					—	$R{-}\ddot{P}X_2$	$R{-}\ddot{P}(OR_2)$
4	+3	H_3PO_3			$R{-}\underset{\underset{O}{\parallel}}{P}X_2$	RPX_4	$R{-}\underset{\underset{O}{\parallel}}{P}(OR)_2$
				—	—	$\ddot{P}X_3$	$\ddot{P}(OR)_3$
5	+5	H_3PO_4		—	$O{=}PX_3$	PX_5	$O{=}P(OR)_3$

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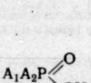
* Those circled by dotted lines are conceivable forms but have not been isolated.

TABLE 2

pK* of phosphorus acids 

A₂ \ A₁	H	C_2H_5O	OH	C_6H_5	C_2H_5
H	1.1	0.81 [8] *	1.42	—	—
C_2H_5O . .	0.81	1.39 [9]	1.6 [9]	—	2.27
OH	1.42 [8]	1.6 [9]	1.97 [9]	2.2 [10]	2.43
C_6H_5 . . .	—	—	2.2	—	—
C_2H_5 . . .	—	2.27	2.43 [6]	—	3.34

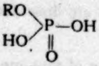
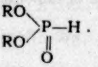
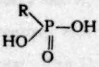
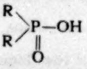
---

* The dissociation constant determined by Nylen seems to us somewhat too high. Probably, this may be explained by slow acid titration. The latter could have resulted in hydrolysis of the ethoxy group.

However, one should not forget in the examination of dissociation constants that they are thermodynamic values characterizing the equilibrium between acid and water. Under these conditions, steric factors and hydration effects should be taken into consideration. However, electron displacement effects are often the main factors.

The same regularity may be observed in comparing the same acids in a homologous series (Table 3).

TABLE 3

Formula	The value R				
	H	CH_3	C_2H_5	C_3H_7	C_4H_9
	1.97 [9]	1.54 [9]	1.60 [9]	1.88 [9]	1.89 [9]
	1.97 [9]	1.29 [9]	1.39 [9]	1.59 [9]	1.72 [9]
	1.42 [8]	2.38 [6]	2.43 [6]	2.41 [6]	2.59 [6]
	1.1	3.08 [6]	3.34, 3.29 [6]	3.46 [6]	3.46 [6] *

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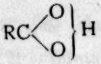
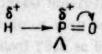
* A certain disparity may be seen in the pK' of dibutylphosphinic acid. This may probably be explained by the fact that Kosolapoff's acid was not very pure and had m.p. 68.5-69° [6], as in his other papers, where the acid was obtained by another method, he gave 71° for its m. p. [7].

The effect of the hydrogen atom directly connected to the phosphorus is noticeable. As a result of it, there is a considerable increase in the dissociation constant in the transition from phosphoric acid to phosphorous and then to hypophosphorous (Table 3). This fact was generally noted in the literature, but, without any explanation, Nylen [8] considers the anomalous effect of the hydrogen connected to phosphorus, as an empirical law. Kumler and Eiler [9] consider that this problem should be treated as a resonance conception.

We consider that the anomalous effect of the hydrogen atom connected to phosphorus is basically similar to the anomalous effect of hydrogen connected to C=O. Due to the semi-polar character of the bonds, the phosphorus and the carbon atom in P=O and C=O possess some positive charge. It should be noted that the formula formerly accepted for these acids  does not, apparently, correspond to the actual acid structure in an un-ionized state. It has been shown electronographically [11] that hydrogen, in an acid molecule, is situated closer to one of the oxygen atoms.

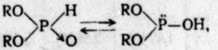
A hydrogen atom, situated near a positively charged phosphorus or carbon atom, also acquires a certain positive charge:  . As a result, a repelling force arises between the hydrogen, on the one hand, and phosphorus or carbon, on the other. Consequently, the bonds become less stable than those in the corresponding PH_3 or CH_4.

Thermodynamic data confirm the existence of such an unstable state of the H−P and H−C bonds. The energy required to break all the formic acid bonds is 433.3 Kcal/mole, while that for acetic acid is 679.6 Kcal/mole [12]. It may be assumed that if the bond energies of the carboxyl group are the same for formic and acetic acids, and there are some indications in the literature to that effect [11], then the bond energy for the H−C bond in formic acid equals 73.6 Kcal/mol while for normal H−C bonds it is 85.6 Kcal/mol [12]. Such a difference in values for bond energy must be outside the limits of error for the roughest thermodynamic data. It is impossible to calculate the bond energy of the H−P bond due to lack of thermodynamic data, but the picture should be analogous.

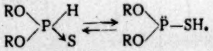
It seems to us that the existence of such energetically unstable bonds as H−P and H−C throws light on such facts as the absence of acid halides of formic and hypophosphorous acids. The anomalously large values for the dissociation constants of formic, phosphorous and hypophosphorous acids are probably also due to this.

The H−P and H−C bonds become somewhat more stable when these acids are dissociated and, as a result, the equilibrium is displaced slightly toward ion formation.

These very same reasons may probably be used to explain also the existence of tautomerism, for example, in dialkylphosphorous acids [13, 14].



as well as in dialkylthiophosphorous acids [15]



This lability of the hydrogen atom in the above acids has been observed and described repeatedly in the literature [16-19].

EXPERIMENTAL

We determined the dissociation constants of two acids − diethylphosphinic and ethoxyethylphosphinic. The first of these had been determined before the appearance of Kosolapoff's work (1953). We found pK' equal to 3.34, which does not differ significantly from Kosolapoff's data (3.29). The acid was prepared from the corresponding acid chloride $(C_2H_5)_2POCl$ by treatment with water. The b. p. was 126° (0.28 mm); according to Kosolapoff's data, the b. p. is 92° (0.08 mm). There is no data in the literature on the second of the acids mentioned above. It was also prepared from the corresponding acid chloride $C_2H_5(C_2H_5O)POCl$, which had the following constants:

b. p. 74-75° at 10 mm, d_4^{20} 1.1631, n_D^{20} 1.4338, MR_D 34.94; Calc. 35.03.

The calculated amount of water was added with stirring to 15 g of acid chloride, which was kept at a low temperature. The hydrogen chloride formed was removed with a stream of nitrogen. After three distillations the acid $C_2H_5(C_2H_5O)POOH$ had:

b. p. 138° (2 mm), d_4^{20} 1.1353, n_D^{20} 1.430, MR_D 31.40; Calc. 31.41.

The dissociation constants were determined by potentiometric titration. Measures were taken to protect the ethoxyl groups from hydrolysis. Samples of acid were dissolved in twice-distilled water, titrated to neutrality of half the acid, and the EMF was determined; as the latter always remained near to unity, the determination was speeded up (less than 1 minute). The pK' value of the acid was determined as 2.27 from 5 parallel experiments.

SUMMARY

1. Ideas on the genetic relation of dialkylphosphinic acids to hypophosphorous acid are put forward.

2. A relation between the dissociation constants of phosphorus-containing acids and their structure has been pointed out.

3. An attempt was made to clarify the following: a) the anomalously high dissociation constants of phosphorous, hypophosphorous and formic acids; b) the absence of acid chlorides of hypophosphorous and formic acids; c) the existence of tautomerism in dialkylphosphorous and dialkylthiophosphorous acids.

4. The pK' values of ethoxyethylphosphinic and diethylphosphinic acids were determined.

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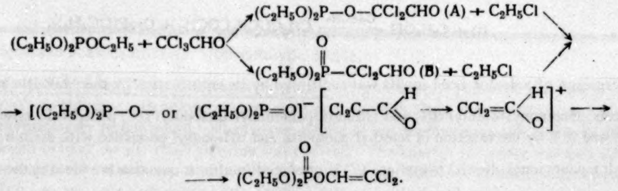
THE ANOMALOUS REACTION OF α-HALOKETONES WITH PHOSPHOROUS ESTERS

IV. THE REACTION OF PHOSPHOROUS ESTERS WITH MONO- AND DICHLOROACETYLACETONE, PHOSPHONOACETONE AND ACETOACETIC ESTER

A. N. Pudovik

In developing our previous investigations of the reactions of triethyl phosphite with monohaloketones [1, 2] and dihaloketones [3], we studied the reactions of phosphorous esters with chloro- and dichloroacetylacetone, acetoacetic ester and phosphonoacetone. It was expected that the existence of an electronegative group near the carbon atom, attached to chlorine, would cause a stronger polarization of the haloketone molecule and as a result of this it would promote an anomalous reaction.

At the present time various opinions have been given on the mechanism of the anomalous reaction of α-haloaldehydes and α-haloketones with phosphorous esters. Perkow, Krockow and Knoevenagel [4] consider that in the first phase of the reaction a molecule of alkyl halide is separated according to the scheme given below; the esteraldehyde formed splits into ions which after rearrangement again combine to give an unsaturated phosphoric ester.

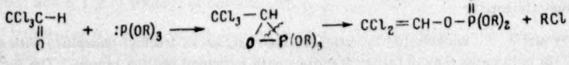


$$(C_2H_5O)_2POC_2H_5 + CCl_3CHO \nearrow (C_2H_5O)_2P{-}O{-}CCl_2CHO\ (A) + C_2H_5Cl \searrow \qquad \searrow (C_2H_5O)_2\overset{O}{\overset{\|}{P}}{-}CCl_2CHO\ (B) + C_2H_5Cl \nearrow$$

$$\longrightarrow [(C_2H_5O)_2P{-}O{-} \text{ or } (C_2H_5O)_2P{=}O]^- \left[Cl_2C{-}C\langle{}^{H}_{O} \longrightarrow CCl_2{=}C\langle{}^{H}_{O}\right]^+ \longrightarrow$$

$$\longrightarrow (C_2H_5O)_2\overset{O}{\overset{\|}{P}}OCH{=}CCl_2.$$

It was previously considered [1] that due to the weakening of the nucleophilic properties of the carbon atom of the carbonyl group in α-halocarbonyl compounds, first the phosphorus atom of the phosphorous ester could add to it and then the electron displacement in both molecules would lead to the formation of an unsaturated phosphoric ester. Allen and Johnson [5] also consider the possibility of the reaction proceeding by this mechanism; however, they consider more probable an initial attack by the nucleophilic phosphorus atom on the electrophilic carbon atom of the carbonyl group; this forms an intermediate product with an oxide ring which decomposes, and an unsaturated phosphoric ester is formed:

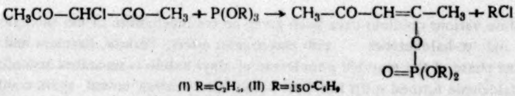


$$CCl_3\underset{\underset{O}{\|}}{C}{-}H + :P(OR)_3 \longrightarrow CCl_3{-}CH\ (O{-}P(OR)_3\ \text{ring}) \longrightarrow CCl_2{=}CH{-}O{-}\overset{O}{\overset{\|}{P}}(OR)_2 + RCl.$$

There is insufficient basis, in our opinion, for the mechanism accepted by Perkow et al. The immediate splitting off of ethyl chloride from triethyl phosphite and chloral with the formation of (A) is improbable. It is also improbable that (B), which, according to the authors, is formed by the usual Arbuzov rearrangement, should decompose with breaking of the phosphorus-carbon bond under the reaction conditions. The difference between the second and third mechanism lies in the fact that, according to the second mechanism, the reaction is supposed to start with attack by the phosphorous ester on the oxygen, while according to the third mechanism – on the carbon atom of the carbonyl group. Considering all the contemporary ideas on the mechanism of reaction of α-haloketones with various reagents [6], we have now come to the conclusion that the reactions of α-halocarbonyl compounds with phosphorous acid esters proceed most probably by the third mechanism, which includes the initial reaction of phosphorous ester with the carbon of the carbonyl group.

There is data in the literature on the reactions of phosphorous esters with the α-bromo derivatives of diketones and acetoacetic ester. The reaction of triethylphosphite and sodium diethyl phosphite with bromodibenzoylmethane and bromotribenzoylmethane proceeds as B. A. Arbuzov and N. P. Bogonostseva [7] had shown, not according to the "Arbuzov" rearrangement scheme, but anomalously, and results in the formation of dibenzoylmethane and tribenzoylmethane, respectively. The authors consider that a radical reaction mechanism is the most probable. Reduction of the dibenzoylmethyl or tribenzoylmethyl to dibenzoylmethane or tribenzoylmethane is caused by hydrogen of the solvent or triethyl phosphite. The triethyl phosphite reacts similarly with bromoindandione. In this case, as well, indandione was produced in good yield.

Triethyl phosphite and triisobutyl phosphite react very readily with chloroacetylacetone, accompanied by a considerable heat effect. Isopentenonyl-diethyl (I) and isopentenonyl-diisobutyl (II) phosphoric esters were obtained in yields of 66 and 80%, respectively:



$$CH_3CO-CHCl-CO-CH_3 + P(OR)_3 \rightarrow CH_3-CO-CH{=}\underset{\substack{| \\ O \\ | \\ O{=}P(OR)_2}}{C}-CH_3 + RCl$$

(I) $R{=}C_2H_5$, (II) $R{=}iso\text{-}C_4H_9$

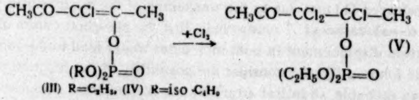
Acetylacetone and triethyl phosphate were obtained by transesterification of (I) with ethyl alcohol in the presence of sodium ethylate.

$$(I) + C_2H_5OH \xrightarrow{C_2H_5ONa} CH_3COCH_2COCH_3 + O{=}P(OC_2H_5)_3.$$

The presence of a double bond in (II) was confirmed by its bromination by the Mak-Ilin method.

Chloroisopentenonyl-diethyl (III) and chloroisopentenonyl-diisobutyl (IV) phosphoric esters were obtained in yields of 63 and 80% by the reaction of triethyl phosphite and triisobutyl phosphite with dichloroacetylacetone.

Trichloropentanonyl-diethyl phosphate (V) is produced in almost quantitative yield by the chlorination of (III):



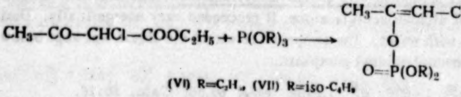
$$CH_3CO-CCl{=}\underset{\substack{| \\ O \\ | \\ (RO)_2P{=}O}}{C}-CH_3 \xrightarrow{+Cl_2} CH_3CO-CCl_2-\underset{\substack{| \\ O \\ | \\ (C_2H_5O)_2P{=}O}}{CCl}-CH_3 \quad (V)$$

(III) $R{=}C_2H_5$, (IV) $R{=}iso\text{-}C_4H_9$

The presence of a double bond in (IV) was confirmed by bromination. Thus the reactions of chloro- and dichloroacetylacetone with phosphorous esters proceed wholly by an anomalous mechanism with the formation of unsaturated phosphoric esters.

B. A. Arbuzov and B. P. Lugovkin [8] investigated the reaction of triethyl phosphite with α- and γ-bromoacetoacetic esters. In both cases they obtained fractions with extended boiling ranges. The authors pointed out the possibility of the formation of either mixtures of keto and enol forms of phosphonoacetoacetic ester or mixtures of isomeric α- and γ-phosphonoacetoacetic esters; the structure of the products obtained was not established.

The reaction between triethyl phosphite and triisobutyl phosphite and α-chloroacetoacetic ester proceeded very readily, starting immediately on mixing the reagents and was accompanied by considerable evolution of heat. Carboxyethylisopropenyl-diethyl phosphate (VI) and carboxyethylisopropenyl-diisobutyl phosphate (VII) were obtained in yields of 91 and 71 %, respectively.



$$CH_3-CO-CHCl-COOC_2H_5 + P(OR)_3 \longrightarrow CH_3-\underset{\underset{\underset{O=P(OR)_2}{|}}{\underset{O}{|}}}{C}=CH-COOC_2H_5$$

(VI) $R=C_2H_5$, (VII) $R=iso\text{-}C_4H_9$

The transesterification of (VI) does not proceed as readily as for (I); acetoacetic ester and triethyl phosphate were identified. The presence of double bonds in (VI) and VII) was established by bromination. Dichloroacetoacetic ester reactions with triethyl and triisobutyl phosphite proceed analogously. It was impossible to determine the double bond quantitatively in carboxyethylchloroisopropenyldiethyl phosphate; bromination proceeded very slowly.

We carried out the chlorination of phosphonoacetone with sulfuryl chloride. Monochlorophosphonoacetone was obtained in a 61% yield. It was impossible to obtain monochlorophosphonoacetophenone and dichlorophosphonoacetone as the reaction mixture became tarry during distillation. Diethylphosphonoisopropenyl-diethyl phosphate was obtained by treating monochlorophosphonoacetone with triethyl phosphate. Diethylphosphonoacetone and triethyl phosphate were obtained in good yields by transesterification with ethyl alcohol in the presence of sodium ethylate.

It is noticeable that the values found for molecular refraction for almost all of the mixed phosphoric esters synthesized are 0.7-1.0 above the calculated values. Exaltation is apparently caused by conjugation of the double carbon-carbon bond with the carbon-oxygen bond in the carboxyl group.

EXPERIMENTAL

Monochloro- and dichloroacetylacetone and monochloro- and dichloroacetoacetic ester were prepared by treating acetylacetone and acetoacetic ester with sulfuryl chloride.

The action of triethyl phosphite on chloroacetylacetone. 37 g of triethyl phosphite was slowly introduced, dropwise, into 30 g of α-chloroacetylacetone, in a round-bottomed flask fitted with a reflux condenser, a dropping funnel and with a thermometer in the liquid. When about a third of the triethyl phosphite had been added, the reaction mixture began to heat up and ethyl chloride was evolved. The triethyl phosphite was then added at such a rate that the temperature of the reaction mixture did not go above 100-110° and at the end of the reaction was not above 140°. After heating on an oil bath at 130-140° for half an hour, the reaction mixture was distilled in vacuum. The main mass of the product distilled at 117-120° at 2 mm. After a second distillation 34.5 g of isopentenonyl-diethyl phosphate was isolated.

B. p. 119-120° at 2 mm, n_D^{20} 1.4489, d_4^{20} 1.1237, MR_D 56.33; Calc. 55.30.

Found %: P 13.09. $C_9H_{17}O_5P$. Calculated %: P 13.13.

Transesterification of isopentenonyl-diethyl phosphate. 0.3 g of sodium was dissolved in 40 ml of anhydrous ethyl alcohol and 18.5 g of isopentenonyl-diethyl phosphate was added to the alcoholate solution obtained. After heating for 2 hours on a water bath, the alcohol was distilled off and the residue was treated with a small amount of water and was extracted with ether. On distillation we obtained 6.3 g of acetylacetone with b. p. 138-139° at 760 mm, n_D^{20} 1.4505 and 5.1 g of triethyl phosphate with b. p. 212-213° at 760 mm, n_D^{20} 1.4085.

The action of triisobutyl phosphite on chloroacetylacetone. The reaction was carried out with 15 g of chloroacetylacetone and 22.2 g of triisobutyl phosphite. On mixing the reagents, the temperature gradually rose to 120° and then began to fall. The reaction mixture was heated at 150° for 30 minutes. During the reaction, 6.2 g of isobutyl chloride was distilled off. Distillation of the reaction mixture gave 25.3 g of isopentenonyl-diisobutyl phosphate.

B. p. 137-138° at 2.5 mm, n_D^{20} 1.4468, d_4^{20} 1.0425, MR_D 74.8; Calc. 73.79.

0.73 g of material: found 0.349 g Br_2; calculated 0.400 g Br_2.

Found %: P 11.01, 10.38. $C_{13}H_{25}O_5P$. Calculated %: P 10.67.

The reaction of triethyl phosphite with dichloroacetylacetone. The reaction was carried out with 25 g of triethyl phosphite and 25 g of dichloroacetylacetone; it proceeded very energetically. During the reaction, the reaction mixture was cooled with water. The temperature within the liquid was kept below 120°. Distillation gave 26.3 g of chloroisopentenonyl-diethyl phosphate.

B. p. 135° at 3 mm, n_D^{20} 1.4626, d_4^{20} 1.2292, MR_D 60.56; Calc. 60.16.

Found %: Cl 13.23; P 11.64, 11.58. $C_9H_{16}O_5ClP$. Calculated %: Cl 13.13; P 11.45.

Chlorination of chloroisopentenonyl-diethyl phosphate. A solution of 13 g of chloroisopentenonyl-diethyl phosphate in 20 ml of carbon tetrachloride was cooled in ice and a slow stream of chlorine was passed through it until 3.5 g had been absorbed. The liquid became yellow. After 2 distillations through a Widmer column, 8.3 g of trichloroisopentehonyl-diethyl phosphate was obtained.

B. p. 151° at 3 mm, n_D^{20} 1.4672, d_4^{20} 1.3431, MR_D 70.54; Calc. 70.36.

Found %: Cl 30.52; P 9.28, 9.17. $C_9H_{16}O_5Cl_3P$. Calculated %: Cl 31.18; P 9.08.

Reaction of triisobutyl phosphite with α, α-dichloroacetylacetone. The reaction was carried out with 11 g of dichloroacetylacetone and 15 g of triisobutyl phosphite; during the reaction the flask was cooled with water. The temperature of the reaction mixture was kept in the range 100-120°. 17.1 g of chlorcisopentenonyl-diethyl phosphate was obtained.

B. p. 150-151° at 4 mm, n_D^{20} 1.4575, d_4^{20} 1.1240, MR_D 79.18; Calc. 78.63.

Found %: Cl 11.02, 10.54. $C_{13}H_{24}O_5PCl$. Calculated %: Cl 10.81; P 9.49.

The action of triethyl phosphite on α-chloroacetoacetic ester. During the addition of 15.2 g of triethyl phosphite to 15 g of α-chloroacetoacetic ester, the temperature of the reaction mixture rose to 120° and was kept at this level until the end of the reaction. Distillation yielded 22.3 g of carboxyethylisopropenyl-diethyl phosphate.

B. p. 155-156° at 10 mm, n_D^{20} 1.4451, d_4^{20} 1.1349, MR_D 62.38; Calc. 61.55.

0.71 g of material: added 0.405 g Br_2; calculated 0.421 g Br_2.

Found %: P 11.77, 11.83. $C_{10}H_{19}O_6P$. Calculated %: P 11.66.

Transesterification of carboxyethylisopropenyl-diethyl phosphate. 10 g of the phosphate ester was heated with a solution of sodium ethylate, prepared from 0.3 g of sodium and 30 ml of ethyl alcohol. After distilling off the alcohol, treating with water, extracting with ether, and distilling, we obtained 3.1 g of acetoacetic ester with b. p. 74-76° at 15 mm, and triethyl phosphate with b. p. 95-99° at 15 mm (2.6 g). Original phosphate ester was isolated from the residue by further distillation. The acetoacetic ester isolated readily gave a semicarbazone with m. p. 129°. A mixed m. p. was not depressed.

Reaction of triisobutyl phosphite with chloroacetoacetic ester. The reaction was carried out with 10 g of chloroacetoacetic ester and 13 g of triisobutyl phosphite. 3.5 g of isobutyl chloride was collected. 14.3 g of carboxyethylisopropenyl-diisobutyl phosphate was obtained.

B. p. 175° at 10 mm, n_D^{20} 1.4445, d_4^{20} 1.0569, MR_D 81.00; Calc. 80.01.

0.76 g of material: added 0.368 g of Br_2: calculated: 0.377 g Br_2.

Found %: P 9.79, 9.90. $C_{14}H_{27}O_6P$. Calculated %: P 9.62.

Reaction of triethyl phosphite with dichloroacetoacetic ester. 10.5 g of triethyl phosphite was added to 12 g of dichloroacetoacetic ester. The reaction proceeded very energetically. The temperature quickly rose to 130°. To decrease the rate, the flask was carefully cooled with warm water. Distillation of the reaction mixture gave 17.5 g of carboxyethylchloroisopropenyl-diethyl phosphate.

B. p. 136° at 1 mm, n_D^{20} 1.4572, d_4^{20} 1.1203, MR_D 67.08; Calc. 66.42.

Found %: P 10.43. $C_{10}H_{18}O_6PCl$. Calculated %: P 10.31.

Reaction of triisobutyl phosphite with dichloroacetoacetic ester. The reaction was carried out with 12.5 g of triisobutyl phosphite and 10 g of dichloroacetoacetic ester. The temperature rose to 120°. During the reaction, 3.8 g of isobutyl chloride was distilled off. 14.5 g of carboxyethylchloroisopropenyl-diethyl phosphate was obtained.

B. p. 154° at 1 mm, n_D^{20} 1.4547, d_4^{20} 1.1289, MR_D 85.63; Calc. 84.69.

Found %: Cl 10.36, 10.46; P 8.95, 8.86. $C_{14}H_{26}O_6PCl$. Calculated %: Cl 9.95; P 8.69.

Chlorination of phosphonoacetone. 11.8 g of sulfuryl chloride was gradually added with stirring to 20 g of phosphonoacetone cooled with ice. The reaction mixture was left to stand over night and then the hydrogen chloride and sulfur dioxide were removed in vacuum. Two distillations from a flask with a small Widmer column gave 14 g of α-chlorophosphonoacetone.

B. p. 131-132° at 9 mm, n_D^{20} 1.4484, d_4^{20} 1.2233, MR_D 50.04; Calc. 50.27.

Found %: Cl 15.90; P 13.81. $C_7H_{14}O_4PCl$. Calculated %: Cl 15.53; P 13.57.

The action of triethyl phosphite on α-chlorophosphonoacetone. The reaction was carried out with 12 g of chlorophosphonoacetone and 10 g of triethyl phosphite with heating. The separation of ethyl chloride began only after the reaction mixture was heated to 100°. On distilling the reaction mixture in vacuum, we isolated 2.5 g of triethyl phosphite, 4.3 g of chlorophosphonoacetone and 6.8 g of diethylphosphonoisopropenyl-diethyl phosphate.

B. p. 161-162° at 1 mm, n_D^{20} 1.4478, d_4^{20} 1.1762, MR_D 75.11; Calc. 75.38.

Found %: P 18.63, 18.73. $C_{11}H_{24}O_7P_2$. Calculated %: P 18.78.

Transesterification of diethylphosphonoisopropenyl-diethyl phosphate. Transesterification of 5 g of diethylphosphonoisopropenyl-diethyl phosphate with 20 ml of ethyl alcohol, in the presence of 0.3 g of sodium ethylate, gave 0.7 g of triethyl phosphite with b. p. 99° at 14 mm and 2 g of diethylphosphonoacetone with b. p. 130-132° at 13 mm; n_D^{20} 1.4330.

SUMMARY

The reactions between the following were investigated: triethyl and triisobutyl phosphites and monochloro- and dichloroacetylacetone, monochloro- and dichloroacetoacetic esters and α-chlorophosphonoacetone. The reactions did not proceed according to the "Arbuzov" rearrangement scheme, but by an anomalous mechanism, with a transfer of reaction center. A number of mixed unsaturated phosphoric esters were obtained in yields of 69-90%.

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INVESTIGATION OF COPOLYMERIZATION OF THREE-COMPONENT SYSTEMS. I.

S. M. Zhivukhin, M. V. Barkova and I. P. Losev

The first examples of copolymerization are described in papers by V. Solonina [1, 2]; however, the copolymerization she describes is exceptional, as one of the reaction components of the systems she was investigating was an inorganic compound – sulfur dioxide. The first copolymerization of two unsaturated organic compounds was observed by I. I. Ostromyslensky [3] who obtained a copolymer based on isoprene and amylenes, and in 1911-1913 he investigated and described the properties of "combined" isopreneamylene rubbers, and put forward a hypothesis on the formation mechanism of these polymers. By now, copolymerization of two unsaturated monomers has been quite thoroughly investigated, but the copolymerization of three and more monomers has been investigated comparatively little.

The aim of this work was to investigate copolymerization in the three-component system methyl methacrylate-acrylonitrile-triallyl borate. We synthesized the third component – triallyl borate $B(OCH_2CH=CH_2)_3$ by the method described in a paper by B. N. Rutovsky and N. S. Leznova [4], by the reaction of boric anhydride with dry allyl alcohol. The product had the following constants:

b. p. 53-54° (2 mm), 67-68° (7.5-8 mm), d_4^{20} 0.915, n_D^{20} 1.4273, MR_D 50.721; Calc. 51.822, bromine number 262.2; Calc. 263.7.

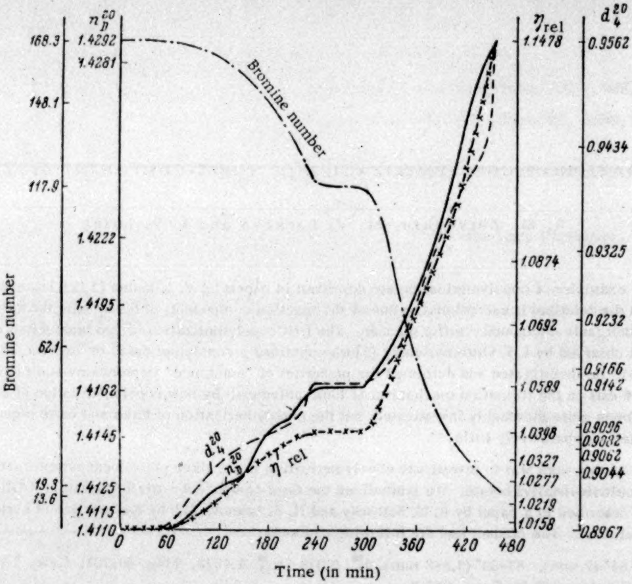
Literature data [4]: b. p. 52-53° (1 mm), d_4^{20} 0.918, bromine number 258.

Notwithstanding the fact that triallyl borate was incapable of polymerization at 60 ± 0.2° in the presence of 0.5% benzoyl peroxide, this ester did copolymerize under these conditions with methyl methacrylate and acrylonitrile; moreover, a transparent, colorless homogeneous block was obtained which did not change during storage.

Special attention was paid to the kinetics of copolymerization as there are no data in the literature on this problem. A triple mixture with molar ratios of the starting components equal to 1:0.1:0.01 was used to study the copolymerization kinetics of the system methyl methacrylate-acrylonitrile-triallyl borate. The investigation results are shown in the figure.

It is possible to prove the existence of several stages of development in the copolymerization process by analysis of the curves. The usual chain polymerization process of vinyl derivatives is characterized by three stages – excitation, growth and breaking of chain, while five stages are observed in the system investigated: 1) induction period lasting 60 minutes (0-60 minutes); 2) growth of copolymer chains, in the following 180 minutes (60-240 minutes); 3) second induction period lasting 60 minutes (240-300 minutes); 4) further growth of copolymer molecules in the following 165 minutes (300-465 minutes); 5) breaking of chain.

In the investigation of the copolymerization kinetics, we determined experimentally the composition of the copolymers obtained at different stages of the copolymerization. For this purpose we analyzed the unreacted monomer mixture for the nitrogen content and triallyl borate. Knowing the composition of this mixture, we compared it with the composition of the original mixture and thus calculated the composition of the copolymer. Besides this, we calculated theoretically the composition of possible copolymers for different stages of reaction by using the differential equations described in the literature [5, 6] for the composition of three component copolymers:



The relation of the refraction index, specific gravity, relative viscosity and bromine number of the system to polymerization time.

$$\frac{dX}{dY}=\frac{\left[\frac{1}{\rho_1}\cdot\frac{1}{\rho_3}X_0Y_0+\frac{1}{\rho_2}X_0\left(\frac{1}{\rho_1}X_0+\frac{1}{\sigma_3}\cdot Z_0\right)\right]\left(X_0+\frac{1}{\sigma_1}Y_0+\frac{1}{\sigma_2}Z_0\right)}{\left[\frac{1}{\sigma_1}\cdot\frac{1}{\rho_2}X_0Y_0+\frac{1}{\rho_3}\cdot Y_0\left(\frac{1}{\sigma_1}Y_0+\frac{1}{\sigma_2}\cdot Z_0\right)\right]\left(Y_0+\frac{1}{\rho_1}X_0+\frac{1}{\sigma_3}Z_0\right)} \tag{1}$$

$$\frac{dX}{dZ}=\frac{\left[\frac{1}{\rho_1}\cdot\frac{1}{\rho_3}X_0Y_0+\frac{1}{\rho_2}X_0\left(\frac{1}{\rho_1}X_0+\frac{1}{\sigma_3}\cdot Z_0\right)\right]\left(X_0+\frac{1}{\sigma_1}Y_0+\frac{1}{\sigma_2}\cdot Z_0\right)}{\left[\frac{1}{\sigma_2}\cdot\frac{1}{\rho_1}\cdot X_0\cdot Z_0+\frac{1}{\sigma_3}\cdot Z_0\left(\frac{1}{\sigma_1}\cdot Y_0+\frac{1}{\sigma_2}\cdot Z_0\right)\right]\left(Z_0+\frac{1}{\rho_2}X_0+\frac{1}{\rho_3}Y_0\right)} \tag{2}$$

Equations (1) and (2) relate the copolymer composition to the composition of the original mixture and to the six relative copolymerization constants for the possible monomer pairs. We determined these copolymerization constants graphically by a method described in the literature [7]. This method gave the following values for the constants: 1) the system methyl methacrylate-acrylonitrile $\sigma_1 = 1.25 \pm 0.07$, $\rho_1 = 0.205 \pm 0.17$; 2) the system methyl methacrylate-triallyl borate $\sigma_2 = 44.8 \pm 3$, $\rho_2 = 0.065 \pm 0.032$; 3) the system acrylonitrile-triallyl borate $\sigma_3 = 37 \pm 0.2$, $\rho_3 = 0.015 \pm 0.006$.

By substituting the values of the relative copolymerization constants in the differential equation of composition we obtained a set of equations which related the composition of the initial copolymer to the composition of the original mixture for the system methyl methacrylate-acrylonitrile-triallyl borate:

$$\frac{x}{y} = \frac{(250X_0Y_0 + 83.33X_0^2 + 0.49X_0Z_0)}{(13.33X_0Y_0 + 40Y_0^2 + 1.11Y_0Z_0)} \cdot \frac{(X_0 + 0.8Y_0 + 0.022Z_0)}{(Y_0 + 5X_0 + 0.027Z_0)}.$$

$$\frac{x}{z} = \frac{(250X_0Y_0 + 83.33X_0^2 + 0.49X_0Z_0)}{(0.111X_0Z_0 + 0.0215Y_0Z_0 + 0.00065Z_0^2)} \cdot \frac{(X_0 + 0.8Y_0 + 0.022Z_0)}{(Z_0 + 16.66X_0 + 50Y_0)}.$$

$$x + y + z = 100 \text{ mole \%}.$$

We calculated copolymer compositions using these three equations. The equations are differential, i.e., allow the determination of the copolymer composition only at the initial moment (with slight reaction) as the values X_0, Y_0 and Z_0 may be considered constant only for such copolymers. Thus, to determine copolymer compositions at any stage of the reaction as well as at the beginning, we used a summation method.

The calculated results correspond satisfactorily with experimentally determined data on the composition of separate copolymer samples at different stages of copolymerization. Some of the results are given in Table 1.

TABLE 1
Polymer Composition (in mole %)

No.	Copolymer yield (in %)	Methyl methacrylate		Acrylonitrile		Triallyl borate	
		Found	Calculated	Found	Calculated	Found	Calculated
3	4.9	92.60	92.75	6.85	7.03	0.55	0.02
4	15.3	92.64	92.87	7.23	7.11	0.13	0.02
5	25.6	92.85	92.77	7.13	7.21	0.02	0.02
6	32.9	92.54	92.70	7.37	7.28	0.09	0.02
7	42.8	92.52	92.58	7.42	7.39	0.06	0.02
8	71.9	92.20	92.21	7.70	7.75	0.09	0.03
9	89.4	91.80	91.56	8.09	8.00	0.06	0.04

TABLE 2

Monomer	Radicals		
	Methyl methacrylate	Acrylonitrile	Triallyl borate
Methyl methacrylate	1	5	15.4
Acrylonitrile	0.8	1	66.6
Triallyl borate	0.022	0.027	1

In this way, the comparison of experimental and theoretical data on copolymer composition obtained at various stages of the reaction, showed that it is possible to calculate theoretically the copolymer composition for the system investigated by us,not only at an early stage of the reaction, but at any stage.

Besides this, from our point of view it is interesting that the copolymer composition varied relatively little for any one of the samples taken during the reaction. As can be seen from data in Table 1, the initial copolymer (test 3) was rich in methyl methacrylate and poor in acrylonitrile and triallyl borate, while the monomer mixture, on the contrary, was poor in acrylonitrile and triallyl borate. Such a ratio of components is the rule in copolymer and monomer mixtures and is maintained for the whole duration of the process, as methyl methacrylate is the most reactive of all three components in copolymerization. This arises from a comparison of the relative activity of the monomers in relation to the free radicals (Table 2).

SUMMARY

1. It was established that triallyl borate is capable of copolymerizing with methyl methacrylate and acrylonitrile in the presence of benzoyl peroxide (0.5%) at 60 ± 0.2%.

2. Kinetics data show that the copolymerization of the system methyl methacrylate-acrylonitrile-triallyl borate has a mechanism differing from the usual polymerization mechanism. This difference lies in the existence of a second induction period in the reaction.

3. The relative copolymerization constants were determined for the systems methyl methacrylate-acrylonitrile, methyl methalcrylate-triallyl borate and acrylonitrile-triallyl borate.

4. By using the three-component system methyl methacrylate-acrylonitrile-triallyl borate as an example, it was shown that theoretical calculation of copolymer composition was possible not only at the beginning, but at any stage of copolymerization.

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INVESTIGATION OF COPOLYMERIZATION OF THREE-COMPONENT SYSTEMS

II. COPOLYMERIZATION OF THE THREE-COMPONENT SYSTEM METHYL METHACRYLATE - ACRYLONITRILE - TETRAALLYL ORTHOSILICATE

S. M. Zhivukhin, M. V. Barkova and I. P. Losev

Tetraallyl orthosilicate [1] was synthesized by treating dry allyl alcohol with silicon tetrachloride. The purified tetraallyl orthosilicate $Si(OCH_2CH=CH_2)_4$ had the following properties:

b. p. 126-127° (26 mm), d_4^{20} 0.9824, n_D^{20} 1.4349, MR_D 68.072; Calc. 68.496. Bromine number 243.3; Calc. 249.4. Literature data [2]: b. p. 115-116° (12 mm), d_4^{20} 0.9842, n_D^{17} 1.4329.

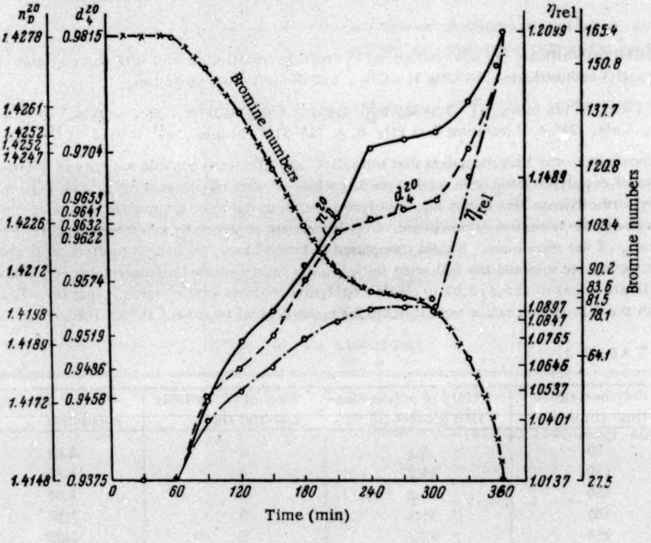
It is known from the literature data that tetraallyl orthosilicate is capable not only of polymerizing by itself but also of copolymerizing with methyl methacrylate or other unsaturated compounds [3]. We established that tetraallyl orthosilicate also enters into copolymerization in the three component system of methyl methacrylate-acrylonitrile-tetraallyl orthosilicate. Copolymers are produced by this three-component system with any initial ratio of the monomers. A solid, transparent, colorless block, unchanged by storage, is obtained by this reaction. However, we selected the following initial molar ratio – methyl methacrylate: acrylonitrile: tetraallyl orthosilicate equal to 1:0.1:0.01 to obtain copolymer products with molding properties. The copolymers obtained with these monomer ratios were suitable for technological treatment at 150-160°.

TABLE 1

Polymerization time (in min.)	Yield of polymerization product (in %)	Amount of insoluble material (in %)	Bromine number of copolymer
90	6.1	0	2.01
120	14.2	0	1.89
150	23.9	0	1.84
180	34.1	0	1.96
210	42.3	0	1.85
240	46.7	3.4	1.64
270	47.4	5.6	0.82
300	47.9	7.3	0.96
330	60.0	39.5	0.1
360	80.1	80.6	0.15
84 hours	100	100	0

We studied the kinetics of the reaction to find out the character and directions of the copolymerization of this three-component system. We followed the copolymerization process by the changes in the refraction index, specific gravity, bromine number, relative viscosity of a 2% polymer solution in acetone and copolymer yield. The polymerization was carried out at 60 ± 0.2° in the presence of 0.5% (of the weight of the mixture) of benzoyl peroxide. The investigation results are shown in the figure.

The same stages of development in the process of copolymer formation as for the system investigated earlier by us – methyl methacrylate-acrylonitrile-triallyl borate [4] – may be found on analysis of the curves, namely: 1) induction period lasting 60 minutes (0-60 minutes); 2) growth of copolymer chain for 180 minutes following the induction period (60-240 minutes); 3) second induction period lasting 60 minutes (240-300 minutes; 4) further growth of copolymer molecules in the following 60 minutes (300-360 minutes); 5) breaking of chain. We determined the solubility and bromine number of the copolymers isolated at different stages in copolymerization to confirm this reaction mechanism for the three-component system investigated. Solubility was determined by extraction with acetone and then with dimethylformamide. The copolymers isolated were saponified with a 1 N alcohol solution of KOH to determine their bromine numbers. The mixture containing the saponification products was diluted with an equal volume of water. The alcohols formed during saponification were distilled off together with the water. The distillate, containing allyl alcohol, was titrated with a bromine solution (T = = 0.0398). The bromine number thus obtained gives the content of allyl groups in the polymer product that did not enter into copolymerization. The analysis results are given in Table 1.



The relation of the values of refractive index, specific gravity, relative viscosity and bromine numbers of the system to polymerization time.

The data on solubility and bromine numbers for 10 copolymer samples (Table 1) show that the copolymers obtained during the first two development stages of copolymerization (induction period, chain growth), have a linear structure as they are characterized by 100% solubility and constancy of bromine number. The copolymers obtained during the following stage, which we call the second induction period, are characterized by an insignificant fall in solubility and bromine number which indicates that a lattice or three dimensional structure starts to form in this period, although this process proceeds very slowly in this case, as can be seen from the changes in the bromine numbers.

As we mentioned above, the third stage is characterized by only the beginning of third dimension formation as the insoluble part in this period consists of only 7.3%. The main formation of lattice or three-dimensional structures takes place in the fourth development stage of copolymerization. In this period up to 80.6% of the insoluble part is formed, while the bromine numbers of the copolymers obtained fall to almost zero (0.1-0.15). The fall in bromine number to zero and the corresponding fall of solubility confirm an hypothesis that the copolymerization process for this system also proceeds in two phases. The first phase is the formation of the copolymer with linear molecular structure using all three original monomers, although the third component of the system – tetraallyl orthoxilicate – reacts with only one allyl group; the second phase is the formation of a copolymer with molecules of a three-dimensional structure from the linear molecules by the reaction of the remaining allyl groups of tetraallyl orthosilicate.

The physicomechanical properties of the copolymer methyl methacrylate-acrylonitrile-tetraallyl orthosilicate. In studying the copolymerization kinetics of the given system we proceeded only as far as 80.1% reaction. The reaction mixture, containing up to 80.1% of polymer product, was hardened further for 84 hours while the initial hardening temperature was kept within the range 35-36° for 24 hours and then gradually raised to 60°, after which the physicomechanical properties of the final copolymer samples obtained were determined. The experimental results are given in Table 2 and it can be seen from it that the copolymers obtained from methyl methacrylate, acrylonitrile and tetraallyl orthosilicate, are characterized by higher hardness, thermostability and electroinsulating properties than polymethyl methacrylate. However, the copolymers obtained are not as water-stable as preparations obtained from polymethyl methacrylate. The copolymers, obtained by us, became dull on the surface when boiled in water for a long time and apparently this may be explained by hydrolysis of the bonds of the Si–O–allyl group, but this defect was eliminated. If the product obtained was treated with moist air or by boiling in solutions of sulfuric or hydrochloric acid followed by thermal treatment in a thermostat at 100-120°, the products' surface remained transparent and unchanged on subsequent boiling in water or acid solutions.

TABLE 2

Characteristics	Triple copolymer (block)	Polymethyl methacrylate
Sample thickness (in mm)	10	10
Specific impact strength ($kg \cdot cm/cm^2$)	13.98	10.1
Yield strength in static bending (kg/cm^2)	513	630
Brinell hardness (kg/mm^2)	18.18	12.3
Thermostability, Marten (°C)	96	55
Water absorption after 24 hours in distilled water (in %)	0.74	0.23
Slope for dielectric losses at 50 cps	$2.0 \cdot 10^{16}$	$1.2 \cdot 10^{13}$
Dielectric permeability at 50 cps	0.019	0.045
	4.7	4.0

SUMMARY

1. Tetraallyl orthosilicate is capable of copolymerization with methyl methacrylate and acrylonitrile. Amounts of not more than 2% of tetraallyl orthosilicate should be introduced into the copolymerization process to obtain copolymers with good outer appearance (transparent, colorless etc.) and molding properties.

2. Kinetics data show that copolymerization of the system methyl methacrylate-acrylonitrile-tetraallyl orthosilicate proceeds in five stages: 1) induction period; 2) copolymer formation, with linear molecular structure; 3) second induction period; 4) formation of three-dimensional copolymers from the linear ones using allyl groups that did not enter into copolymerization during the second stage; 5) breaking of chain.

3. It was established that copolymerizing acrylonitrile and tetraallyl orthosilicate with methyl methacrylate resulted in the formation of products with high hardness, thermostability and electroinsulating properties but with low water stability in comparison with methyl methacrylate polymer.

4. A method is given for raising the water stability of the copolymer products.

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INVESTIGATION OF COPOLYMERIZATION OF THREE-COMPONENT SYSTEMS

III. COPOLYMERIZATION OF THE SYSTEM METHYL METHACRYLATE - ACRYLONITRILE - GLYCOL ESTERS OF METHACRYLIC ACID

S. M. Zhivukhin, M. V. Barkova and I. P. Losev.

For studying the effect of the chain length of cross-linking agents on the copolymerization kinetics and the properties of the copolymer products obtained, we synthesized the following glycol esters of methacrylic acid: glycol dimethacrylate, 1,4-butylene glycol dimethacrylate and diethylene glycol dimethacrylate.

EXPERIMENTAL

Glycol dimethacrylate was prepared by treating glycol with methacrylic acid [1]. We used the following conditions for the synthesis: 104.3 g (1.2 moles) of freshly distilled methacrylic acid was mixed with 31.03 g (0.5 mole) of vacuum-distilled ethylene glycol and to the mixture was added 2 g of concentrated sulfuric acid (d 1.84), 25 g of hydroquinone, which had been recrystallized from water, and 50 ml of anhydrous benzene. The reaction mixture was heated in a three-necked flask for 2 hours at 97-103°. The water which formed was continuously distilled off with benzene and was collected in a Dean and Starke trap. The end of the reaction was indicated when no more water separated out in the trap. During the reaction, a continuous stream of dry nitrogen was passed through the mixture. When the reaction was complete, the mixture was cooled in the stream of nitrogen, treated with anhydrous sodium bicarbonate to neutralize the sulfuric acid,and filtered. The filtrate was dried for 24 hours over fused calcium chloride and distilled in vacuum in a stream of nitrogen; a fraction was collected which boiled in the range 98-100° (4-5 mm). The yield of ester was 55-60 %, calculated on ethylene glycol. The ester was purified from hydroquinone by the usual method. The constants of glycol dimethacrylate are given in Table 1.

TABLE 1

Ester	Boiling point (mm)	d_4^{20}	n_D^{20}	MR_D		Saponification number		Bromine number *	
				found	calculated	found	calculated	found	calculated
Glycol dimethacrylate	98-100°(4-5) 103-105 (8-9)	1.0508	1.4549	51.72	50.75	565.7	565.5	160.8	161.25
1,4-Butyleneglycol dimethacrylate	132-134 (4-5)	1.0227	1.4570	60.26	59.99	485.3	494.9	138.9	141.4
Diethyleneglycol dimethacrylate	150-152 (7-8)	1.0821	1.4685	62.19	61.63	462.0	462.8	131.5	132.07

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* The bromine numbers of the methacrylic esters were determined by Bromination [3].

1,4-Butyleneglycol dimethacrylate was prepared by an analogous method. 90 g (1 mole) of 1,4-butyleneglycol was mixed with 206.4 g (2.4 moles) of methacrylic acid, 25 g of hydroquinone, 2 g of sulfuric acid and 50 ml of anhydrous benzene. The initial temperature of the reaction was 102° and the final 135°. The reaction took 7 hours. After neutralization, the mixture was distilled in vacuum at 4-5 mm; a fraction with b. p. 132-134° was collected. The yield of ester was 50-55 %, calculated on 1,4-butylene glycol. After purification from hydroquinone, the ester had the constants given in Table 1.

Diethyleneglycol dimethacrylate was prepared by transesterification of methyl methacrylate with diethyleneglycol. 106 g (1 mole) of diethyleneglycol, 500 g (5 moles) of methyl methacrylate, 3 ml of sulfuric acid (d 1.84) and 25 g of hydroquinone were mixed carefully and the reaction mixture was heated for 5-6 hours at 118-120°. The methyl alcohol produced by the diethyleneglycol reacting with the methyl methacrylate was distilled off continuously with excess methyl methacrylate as an azeotropic mixture boiling at 65°. After isolation of 120 ml of this mixture, the synthesis was considered complete. After cooling, the reaction mixture was neutralized with sodium bicarbonate, filtered, dried and distilled in vacuum. A fraction with b. p. 150-152° (7-8 mm) was collected. The yield of ester was 60%, calculated on diethyleneglycol. Its constants are given in Table 1.

Copolymerization of the three-component system methyl methacrylate – acrylonitrile – glycol esters of methacrylic acid by the block method. It is known from literature data that glycol dimethacrylate is capable not only of polymerizing alone but also of copolymerizing with methyl methacrylate [1, 2]. However, there is no mention in the literature of copolymerization of glycol dimethacrylate in three-component systems. There are no data at all on the polymerization or copolymerization of 1,4-butyleneglycol dimethacrylate or diethyleneglycol dimethacrylate. We determined that all the esters mentioned would copolymerize with methyl methacrylate and acrylonitrile with all three components present in the system, and that the triple mixture methyl methacrylate – acrylonitrile – glycol esters of methacrylic acid copolymerized in all proportions. Increasing the amount of glycol methacrylates or decreasing the amount of methyl methacrylate and acrylonitrile in the mixture, slowed down the copolymerization process. Of all the copolymers prepared, only the copolymer containing 0.01 mole of glycol methacrylates to 1 mole of methyl methacrylate was capable of being worked (molded) at 160-180°.

Reaction kinetics of copolymerization of the three-component system methyl methacrylate – acrylonitrile – glycol dimethyl methacrylate. The reaction was carried out in sealed ampules at 60 ± 0.1° in the presence of benzoyl peroxide (0.5% on the weight of the monomer). Two ampules were withdrawn every half hour. After being opened, the contents of one of the ampules were distilled in vacuum (2 mm) to separate the monomer from the polymer. The refractive index, specific gravity and bromine number were determined for the monomer. The contents of the second ampule were treated with methyl alcohol to precipitate the polymeric product. The latter was washed many times with methyl alcohol and ethyl ether and after that it was dried to constant weight in vacuum (21 mm) at room temperature. The analytical data in Table 2 shows that the copolymerization reaction in the three-component system methyl methacrylate – acrylonitrile – glycol dimethacrylate proceeds in three steps. In the system investigated we did not find the second induction period, which is characteristic of the system methyl methacrylate – acrylonitrile – triallyl borate [4] or tetraallyl orthosilicate [5]. By the methods which we used for this system, we could not detect the presence of copolymers with linear structures. The polymers isolated at various stages of the reaction were almost completely insoluble in acetone and dimethylformamide. The bromine

TABLE 2

Time of polymerization	Bromine number	Polymer yield (in %)	Time of polymerization	Bromine number	Polymer yield (in %)
0	166.6	0	510	172.8	11.15
120	166.4	0	540	175.9	26.7
240	166.8	0	570	178.3	29.3
420	169.3	5.88	630	181.7	42.8
480	171.5	9.51	72hours	—	100

numbers of these polymers were zero. These data indicate that the copolymerization of the given system forms copolymers with almost exclusively three-dimensional structures, which can only occur if both methacrylate groups take part almost simultaneously in the building up of the copolymer molecule.

The analytical data on the refractive index, specific gravity and bromine number for the mixture of monomers isolated at various stages of the reaction indicated that the composition of the mixture did not remain constant during the reaction.

In studying the kinetics of the reaction we observed some increase in all the kinetic constants. This change was completely regular and, in our opinion, was due to the following. Methyl methacrylate, of all the three components, has the greatest reactivity for copolymerization in the three-component system. Data on the reactivity of methyl methacrylate and acrylonitrile toward both radicals, show that the methyl methacrylate monomer reacts with the methyl methacrylate radical 1.25 times as fast as acrylonitrile and with the acrylonitrile radical, 5 times as fast. Consequently, methyl methacrylate, as the more reactive monomer, will be used up more rapidly in the reaction, and the monomer mixture will have a smaller percent of methyl methacrylate during the reaction, i.e., it will be poor in the more reactive component and correspondingly rich in a less reactive monomer, such as glycol dimethacrylate. The increase in the percent of glycol dimethacrylate also explains some growth in the kinetic indices of the monomer mixture.

Copolymerization of the system methyl methacrylate – acrylonitrile – glycol esters of acrylic acid by the emulsion method makes it possible to use copolymers based on the three monomers: methyl methacrylate, acrylonitrile and glycol esters of methacrylic acid, as molding compositions for making products with increased chemical resistance to solvents. We carried out copolymerizations of the given system by the emulsion method with this aim. For copolymerization we used the same molar proportions as for block polymerization (1:0.1:0.01). In carrying out emulsion copolymerization, it was established that to obtain copolymers containing 4.95% of acrylonitrile (which corresponds to the molar proportions 1:0.1:0.01), it was necessary to take excess acrylonitrile (0.5 mole of acrylonitrile to 1 mole of methyl methacrylate).

TABLE 3

Name of material	Mechanical properties			Electrical insulation	
	Specific impact strength (kg · cm/cm²)	Brinell hardness (kg/mm²)	Thermo-stability – Martens	Specific volume resistance (ohm/cm²)	Slope for dielectric losses at 50 cps
	Block products				
M–AN–GM	8.7	19.91	92°	$2.0 \cdot 10^{13}$	0.037
M–AN–1,4-BDM	9.3	17.4	92	$2.4 \cdot 10^{13}$	0.038
M–AN–DGM	10.4	17.5	88	$1.8 \cdot 10^{13}$	0.032
M	10.1	12.3	55	$1.2 \cdot 10^{13}$	0.045
	Emulsion products				
M–AN–GM	3.71	22.4	86	$1.3 \cdot 10^{15}$	0.023
M–AN–1,4-BDM	4.33	19.28	86	$1.8 \cdot 10^{14}$	0.037
M–AN–DGM	4.96	18.44	80	$1.2 \cdot 10^{14}$	0.041
M	5.5–6	12	50	$2.6 \cdot 10^{14}$	0.055

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* M) methyl methacrylate, AN) acrylonitrile, GM) glycol dimethacrylate, 1,4-BDM) 1,4-butyleneglycol dimethacrylate, DGM) diethyleneglycol dimethacrylate.

The copolymerization of the above monomers was carried out in a water emulsion with a ratio of water to monomer mixture of 2:1. In this experiment, a mixture was prepared consisting of 200.22 g (2 moles) of methyl methacrylate, 53.05 g (1 mole) of acrylonitrile and 0.02 mole of glycol esters of methacrylic acid. 1.286 g of benzoyl peroxide (0.5% of the weight of the mixture) was dissolved in the mixture obtained. The mixture of monomers with the initiator was emulsified in 500 ml of water containing 5.14 g of starch (2% of the weight of the monomer mixture). Dibutyl phthalate (5% of the weight of the mixture) was used as plasticizer. Emulsification was carried out for 10 minutes with vigorous stirring (1200 rev/min); the pH of the mixture was 7. The temperature of the mixture was slowly raised to 76° on a water bath. This took 3 hours. The reaction mixture was kept at 74-76° for 2.5-3 hours until the copolymer was formed, the latter was freed from emulsifier by washing with water until the washings gave no blue color with iodine solution. The washed copolymer was dried at 56-60° and passed through sieve No. 30 (900 holes/cm^2; 75 mesh). Standard blocks and discs were molded from the copolymer obtained. The conditions of molding for these copolymers was as follows: temperature 190-200°, specific pressure 300 kg/cm^2, time in the mold 20 minutes, the molds were cooled to 100° before the products were removed from them. The results of physicomechanical testing of the block and emulsion copolymers are given in Table 3.

SUMMARY

1. The copolymerization of methyl methacrylate and acrylonitrile with glycol esters of methacrylic acid results in the formation of infusible and insoluble products.

2. The copolymerization mechanism of the system methyl methacrylate – acrylonitrile – glycol dimethacrylate is different from the copolymerization mechanism of systems containing allyl derivatives. The copolymerization of the given system proceeds in three stages: induction period, formation of a three dimensional copolymer due to the simultaneous reaction of both methacrylic groups of the glycol derivatives and breaking of the chain.

3. The triple copolymers mentioned may be obtained by block or water emulsion methods. In the first case the initial monomers may be taken in any ratio, while in the second the introduction of from 1.75 to 2.25% of cross-linking additions are recommended.

4. Products may be obtained from these copolymers with higher hardness, heat-resistance and stability to organic solvents than products based on polymethyl methacrylate.

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SULFONATION OF 2-CHLORONAPHTHALENE

II. SULFONATION AT ELEVATED TEMPERATURE[*]

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When 2- chloronaphthalene was heated with sulfuric acid monohydrate (1.5 moles of H_2SO_4 per mole of 2-chloronaphthalene) at 160-165° for 3 hours we obtained a substantial amount of 2-chloronaphthalene-6-sulfonic acid (~80%) and small amounts of 2-chloronaphthalene-8-sulfonic acid (~3%) and 2-chloronaphthalene-6,8-disulfonic acid (~10%) (Expt. 1). An increase in the amount of monohydrate to 3 moles of H_2SO_4 per mole of 2-chloronaphthalene under the same conditions led to an increase in the amount of 2-chloronaphthalene-6,8-disulfonic acid (~40%) and a corresponding decrease in the amount of 2-chloronaphthalene-6-sulfonic acid (~60%) (Expt. 2). When the time of sulfonating 2-chloronaphthalene with the monohydrate was increased to 19 hours we were able to establish the formation of 2-chloronaphthalene-7-sulfonic acid, the presence of which had not been revealed in the earlier sulfonation of 2-chloronaphthalene (Expt. 3). Evidently, 2-chloronaphthalene-7-sulfonic acid is a transformation product of 2-chloronaphthalene-6-sulfonic acid, since it can also be obtained by heating the anhydrous potassium salt of 2-chloronaphthalene-6-sulfonic acid with oil of vitriol at 160° for 15 hours (Expt. 4).

The separation of the mixture of sulfonation products, containing 2-chloronaphthalene-6- and 2-chloronaphthalene-7-sulfonic acids, is extremely difficult due to the small differences in the solubilities of their salts and derivatives, and also due to the formation of secondary products (probably sulfones and oxidation products) under these sulfonation conditions.

EXPERIMENTAL

Isolation of sulfonation products. On conclusion of sulfonation, the sulfonation mass was poured into a mixture of water and ice and then neutralized with potash; the unreacted 2-chloronaphthalene was removed by filtration. The solution of the sulfonic acid potassium salts was then fractionally crystallized by evaporation. If the fraction contained a large amount of mineral impurities, then the sulfonic acid potassium salts were extracted from the mixture with hot alcohol. After this, the air-dried potassium salt fractions were converted to the sulfonyl chlorides, as described earlier [1]. Prolonged sulfonation led to a darkening of the sulfonation mass; the precipitates of the sulfonic acid potassium salts were of a brown color, while the viscous and dark chlorides obtained from them were difficult to crystallize. By employing the technique of fractional crystallization from glacial acetic acid we were able to separate the low-melting, more soluble portion from the mixed chlorides, which was then converted into anilides. After repeated recrystallization of the mixed anilides from dichloroethane and alcohol we obtained an anilide as rectangular plates, characteristic for the anilide of 2-chloronaphthalene-7-sulfonic acid, m.p. 144.5-145°; the mixed melting point of this anilide with authentic 2-chloronaphthalene-7-sulfanilide was not depressed.

Sulfonation of 2-chloronaphthalene with the monohydrate at 160°. Experiment 1. To 9.8 g of molten 2-chloronaphthalene (0.06 mole) was added 8.8 g of 100% monohydrate (0.09 mole); the mixture was held at 160-165° for 3 hours. The mass congealed when cooled to 37°. On working up the sulfonation mass we recovered 0.30 g of 2-chloronaphthalene and obtained 8 fractions of sulfonic acid potassium salts.

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[*] For Communication I see [1].

The first fraction (0.70 g) gave 0.62 g of the chloride, which was converted into the anilide with m.p. 120.5°. From the 2nd fraction (5.30 g) 3.0 g was converted into 2.75 g of chloride, the fractional crystallization of which from glacial acetic acid gave two chloride fractions with m.p. 110° (the anilides prepared from them had m.p. 121-121.5°). From 3.0 g of the 3rd fraction (total 4.30 g) we obtained 2.90 g of chloride, two fractions of which after fractional crystallization had m.p. 110 and 108-108.7°. From 1.1, 1.2 and 1.27 g of potassium salts from the 4th, 5th and 6th fractions we respectively obtained 0.94, 1.10 and 1.0 g of chlorides with m.p. 107-108, 110 and 109.5°. The mixed melting points of all these fractions of chlorides and anilides with the chloride and anilide of 2-chloronaphthalene-6-sulfonic acid were not depressed. From the 7th fraction, containing a large amount of mineral impurities, extraction with hot alcohol gave 0.94 g of a potassium sulfonate, which was converted into 0.52 g of chloride with m.p. 128-129.5° (its mixed melting point with 2-chloronaphthalene-8-sulfonyl chloride was 130-130.5°). From the 8th fraction of potassium salts (3.65 g) we obtained a low-melting chloride, from which by repeated recrystallization a product with m.p. 169-170.5° was isolated (its mixed melting point with 2-chloronaphthalene-6,8-disulfonic acid was 171-172°). Consequently, the mixture of sulfonation products contained 2-chloronaphthalene-6-sulfonic acid (~80%), 2-chloronaphthelene-8-sulfonic acid (~3%) and 2-chloronaphthalene-6,8-disulfonic acid (~10%).

Experiment 2. To 9.8 g of 2-chloronaphthalene was added 17.6 g of 100% monohydrate; sulfonation at 160-165° was maintained for 3 hours. The cooled mass remained mobile. Two fractions (11.19 and 1.72 g of 2-chloronaphthalene-6-sulfonic acid potassium salts were obtained, which were converted into chlorides (8.18 and 0.72 g), from which fractional crystallization gave only the 2-chloronaphthalene-6-sulfonyl chloride with m.p. 110° (amide, m.p. 184.2-184.8°). From the 3rd fraction of potassium salts, containing mineral impurities, extraction with hot alcohol gave 0.9 g of potassium salt, which was converted into 0.83 g of chloride with m.p. 172-172.3° (its mixed melting point with 2-chloronaphthalene-6,8-disulfonyl dichloride was 172.8°). The last two fractions (5.32 and 8.39 g) proved to be the potassium salt of 2-chloronaphthalene-6,8-disulfonic acid; the dichlorides (1.77 and 5.26 g) obtained from them had m.p. 167-167.6 and 172.6-173°, respectively. As a result here the sulfonation mass contained about 60% of 2-chloronaphthalene-6-sulfonic acid and about 40% of 2-chloronaphthalene-6,8-disulfonic acid. 2-Chloronaphthalene-8-sulfonic acid was not found.

Prolonged sulfonation of 2-chloronaphthalene with the monohydrate at elevated temperature. Experiment 3. To 9.8 g of 2-chloronaphthalene was added 11.8 g of 100% monohydrate; stirring at 160-165° was maintained for 19 hours. The sulfonation mass was dark, and the solution of the sulfonation mass in water was dark, turbid, and filtered with difficulty. Three fractions of sulfonic acid potassium salts were obtained. The precipitates had a brown color; the chlorides were viscous, brown, and crystallized with difficulty. From the 1st fraction of potassium salts (9.44 g) we obtained 7.60 g of chloride. The low-melting portion of the mixed chlorides, insoluble in glacial acetic acid, was converted into a low-melting anilide, the melting point of which after repeated recrystallization from dichlorethane and alcohol was 142.5-144° (its mixed melting point with 2-chloronaphthalene-7-sulfanilide was 144-145°); under the microscope the crystals of the anilide appeared as rectangular plates. The portion of the mixed chlorides, showing slight solubility in glacial acetic acid, was converted into the anilide, from which by fractional crystallization from alcohol we obtained 4 fractions with m.p. 120-121° (the mixed melting points of the different fractions with 2-chloronaphthalene-6-sulfanilide were not depressed); under the microscope these anilide fractions appeared as flat needles. The portion of mixed chlorides, showing a greater solubility in glacial acetic acid, was converted into the anilide, which after recrystallizations from dichloroethane and alcohol had m.p. 142.5-143.5° (its mixed melting point with authentic 2-chloronaphthalene-7-sulfanilide was 145-146°). The 2nd fraction proved to contain a large amount of mineral impurities. Extraction with hot alcohol gave 3.6 g of potassium salts, which were converted into 2.2 g of low-melting chloride. The chloride was converted into a low-melting anilide, from which recrystallizations from dichloroethane and alcohol gave a product with m.p. 142-142.5° (its mixed melting point with 2-chloronaphthalene-7-sulfanilide was 145-146°). From the 3rd fraction of 10.52 g of potassium salts we obtained 4.8 g of low-melting chloride, which was converted into a low-melting anilide. After recrystallizations from dichloroethane and alcohol, m.p. 144.5-145°, its mixed melting point with 2-chloronaphthalene-7-sulfanilide was 145-146°. The main components of the 1st fraction of potassium salts are 2-chloronaphthalene-6- and 2-chloronaphthalene-7-sulfonic acids (a total of ~48%), while in the 2nd and 3rd fractions the main component is 2-chloronaphthalene-7-sulfonic acid (~44%).

Isomerization of 2-chloronaphthalene-6-sulfonic acid into 2-chloronaphthalene-7-sulfonic acid. Experiment 4. A stirred mixture of 8.44 g of anhydrous potassium 2-chloronaphthalene-6-sulfonate (0.03 mole) and 15.8 g of 93% oil of vitriol (14.7 g H_2SO_4, 0.15 mole) was heated at 155-160° for 15 hours. From the 1st fraction of potassium salts (4.57 g) we obtained 2.57 g of chlorides. The low-melting portion of the mixed chlorides, insoluble in glacial acetic acid, was converted into the amide, which after recrystallization from aqueous alcohol had m.p. 174-175° (its mixed melting point with 2-chloronaphthalene-7-sulfamide was 175.6-176°). The portion of mixed chlorides, soluble in glacial acetic acid, was also converted into the amide, which after recrystallization had m.p. 184-184.5° (its mixed melting point with 2-chloronaphthalene-6-sulfamide was 185°). From the 2nd fraction, containing many mineral impurites, extraction with hot alcohol gave 3.0 g of potassium salts, which were converted into chlorides (2.0 g). The chlorides were converted into amides, from which by fractional crystallization we obtained two amide fractions with m.p. 175-176° (its mixed melting point with 2-chloronaphthalene-7-sulfamide was 177°) and 185° (its mixed melting point with 2-chloronaphthalene-6-sulfamide was 185.3°). From the 3rd fraction of potassium salts (3.87 g) we obtained 1.35 g of chloride, which after recrystallization had m.p. 172° (its mixed melting point with authentic 2-chloronaphthalene-6,8-disulfonyl dichloride was 172.5°). The chloride (0.77 g) from the 3rd fraction of potassium salts (5.01 g) after recrystallization had m.p. 168-169°; its mixed melting point with 2-chloronaphthalene-6,8-disulfonyl dichloride was 170-171°. The main components of the 1st and 2nd fraction of potassium salts are 2-chloronaphthalene-6- and 2-chloronaphthalene-7-sulfonic acids (a total of ~ 58%), while the main component of the 3rd and 4th fractions is 2-chloronaphthalene-6,8-disulfonic acid (~ 19%).

SUMMARY

1. The main products of the short (3 hour) sulfonation of 2-chloronaphthalene with sulfuric acid monohydrate at 160-165° are mainly 2-chloronaphthalene-6-sulfonic acid with small amounts of 2-chloronaphthalene 8-sulfonic acid and 2-chloronaphthalene-6,8-disulfonic acid.

2. The prolonged sulfonation (19 hours) of 2-chloronaphthalene with the monohydrate at 160° gives, together with 2-chloronaphthalene-6-sulfonic acid, 2-chloronaphthalene-7-sulfonic acid, the presence of which had not been revealed in the earlier sulfonation of 2-chloronaphthalene.

3. Prolonged exposure of the potassium salt of 2-chloronaphthalene-6-sulfonic acid to the action of oil of vitriol at 160° results in its partial isomerization to the 2-chloronaphthalene-7-sulfonic acid.

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SULFONATION OF 2-CHLORONAPHTHALENE

III. TWO-STEP SULFONATION WITH MONOHYDRATE AND OLEUM

N. N. Vorozhtsov, Jr. and N. N. Karandasheva

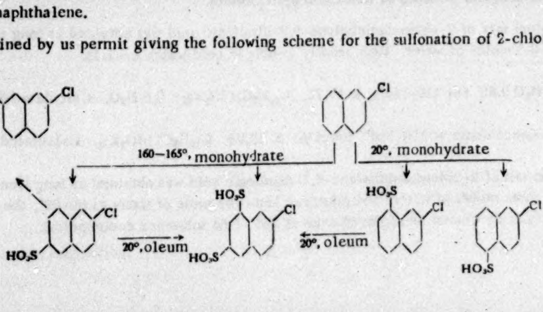
Armstrong and Wynne obtained the disulfonic acids of 2-chloronaphthalene from the anhydrous potassium salts of the monosulfonic acids by heating them at 100° with 20% oleum [1]. They obtained in this manner: from 2-chloronaphthalene-8-sulfonic acid the 2-chloronaphthalene-6,8-disulfonic acid; from the 5-sulfonic acid, the 5,7-disulfonic acid; from the 6-sulfonic acid, the 6,8-disulfonic acid with a small amount of the 4,6-disulfonic acid; and from the 7-sulfonic acid, the 4,7-disulfonic acid. 2-Chloronaphthalene-6,8-disulfonic acid was also obtained by Arnell by the action of excess oleum on 2-chloronaphthalene at 160-180° [2].

We obtained the 2-chloronaphthalene-6,8-disulfonic acid by treating the sulfonation mass of variable composition, obtained in the sulfonation of 2-chloronaphthalene with the monohydrate, with 19% oleum in the cold. Starting with the sulfonation mass, containing 70% 2-chloronaphthalene-8-sulfonic acid and 30% 2-chloronaphthalene-5-sulfonic acid (obtained by the sulfonation of 2-chloronaphthalene with the monohydrate at 20° [3]), we obtained as the main reaction product 2-chloronaphthalene-6,8-disulfonic acid (~98%) with a small amount of 2-chloronaphthalene-5,7-disulfonic acid (~2%). Consequently, under these conditions 2-chloronaphthalene-6,8-disulfonic acid is formed from both the 8-sulfonic acid and the 5-sulfonic acid of 2-chloronaphthalene. It is possible that the 2-chloronaphthalene-5-sulfonic acid is first converted into either the 6- or the 8-sulfonic acid.

Starting with the sulfonation mass, containing 80% 2-chloronaphthalene-6-sulfonic acid, 3% 2-chloronaphthalene-8-sulfonic acid, 10% 2-chloronaphthalene-6,8-disulfonic acid and 3% unchanged 2-chloronaphthalene (obtained by the sulfonation of 2-chloronaphthalene with the monohydrate at 160° [4]), we obtained the 2-chloronaphthalene-6,8-disulfonic acid in nearly quantitative yield. Here we were unable to detect any other isomers, including the 2-chloronaphthalene-4,6-disulfonic acid indicated by Armstrong and Wynne.

It should be mentioned that the arguments presented by Armstrong and Wynne for the formation of the 2-chloronaphthalene-4,6-disulfonic acid are not convincing. The authors attempted to prove the formation and structure of this disulfonic acid from the melting point of its dichloride (148°), failing to determine the melting point of its mixture with the 2-chloronaphthalene-4,6-disulfonyl dichloride obtained by counter synthesis. The conversion of the dichloride with m.p. 148° into 1,3,7-trichloronaphthalene is not proof for the presence of 2-chloronaphthalene-4,6-disulfonic acid, since the 2-chloronaphthalene-6,8-disulfonyl dichloride also converts into 1,3,7-trichloronaphthalene.

The data obtained by us permit giving the following scheme for the sulfonation of 2-chloronaphthalene:



As in the case of 2-methylnaphthalene, in the sulfonation of 2-chloronaphthalene to the mono- and disulfonic acids the sulfo group does not enter the ring already containing a substituent. Here in the cold the sulfo group enters both of the α-positions of the unsubstituted ring and in this connection mainly the quinogenic 8 position (in accord with the Vesely and Jakes rule) [5]. The 2-chloronaphthalene-6-sulfonic acid formed at elevated temperature is transformed into the 2,7-isomer when the time of sulfonation is increased. It is necessary to mention that the 2-chloronaphthalene-6-sulfonic acid is also formed when the sulfonation is run for a very long time at low temperature. The formation of the 2-chloronaphthalene-5- and 2-chloronaphthalene-7-sulfonic acids in the sulfonation of 2-chloronaphthalene had not been observed earlier. At the same time we were unable to show the formation of 2-chloronaphthalene-4,6-disulfonic acid, described earlier as a sulfonation product.

EXPERIMENTAL

Experiment 1. To 70.6 g of 100% sulfuric acid monohydrate (0.72 mole) with stirring was gradually added 19.6 g of 2-chloronaphthalene (0.12 mole). The stirring at 20° was continued for 3 hours. Then to the sulfonation mass was added 54.1 g of 57.7% oleum (32.1 g of free SO_3, 0.39 mole;; the initial concentration of free SO_3 in the sulfonation mixture was 18.8%), and the mass was held at 0° for 1 hour. Then the sulfonation mass was poured into a mixture of water and ice, and neutralized with potash. Evaporation of the solution gave three fractions of sulfonic acid potassium salts. The weight of the 1st fraction of potassium salts was 7.90 g; from 4.00 g we obtained 3.2 g of chloride. After fractional crystallization from glacial acetic acid two of the chloride fractions had m.p. 173 and 170-171°; their mixed melting points with authentic 2-chloronaphthalene-6,8-disulfonyl dichloride were 173 and 172°, respectively. The weight of the 2nd fraction of potassium salts was 28.5 g; from 3.00 g we obtained 2.35 g of chlorides. The portion of mixed chlorides, less soluble in glacial acetic acid, weighed 1.14 g and had m.p. 171.7-172° (its mixed melting point with authentic 2-chloronaphthalene-6,8-disulfonyl dichloride was 172.5°). The portion of mixed chlorides, more soluble in glacial acetic acid, weighed 0.04 g and had m.p. 148-150°; its mixed melting point with authentic 2-chloronaphthalene-5,7-disulfonyl dichloride was 153-155°. The weight of the 3rd fraction of potassium salts was 15.0 g; from 3.00 g we obtained 2.25 g of chlorides. The portion of mixed chlorides, less soluble in glacial acetic acid, weighed 0.99 g and had m.p. 168-170.5°; its mixed melting point with 2-chloronaphthalene-6,8-disulfonyl dichloride was 171-172°.

The portion of mixed chlorides, more soluble in glacial acetic acid, weighed 0.02 g and had m.p. 155-156°; its mixed melting point with 2-chloronaphthalene-5,7-disulfonyl dichloride was 156.5°. The main component of the 1st, 2nd and 3rd fractions of potassium salts is the 2-chloronaphthalene-6,8-disulfonic acid (~98%); the 2nd and 3rd fractions were found to contain a small amount of 2-chloronaphthalene-5,7-disulfonic acid (~ 2%).

Experiment 2. To 19.6 g of molten 2-chloronaphthalene was added 17.6 g of 100% monohydrate; stirring at 160-165° was maintained for 3 hours. To the sulfonation mass, cooled to 40°, was added 33.28 g of 57.7% oleum (initial concentration of free SO_3 in the sulfonation mixture was 18.9%), and the sulfonation was continued at 20° for 2 hours. Then the sulfonation mass was poured into a mixture of water and ice, and neutralized with potash. Evaporation of the solution of potassium salts gave three fractions, which were converted into the sulfonyl chlorides (total weight 41.11 g). After fractional crystallization from glacial acetic acid we obtained ten fractions, of 2-chloronaphthalene-6,8-disulfonyl dichloride; the melting points ranged from 168 to 173°; we were unable to show the presence of other sulfonyl chlorides.

The potassium salt of 2-chloronaphthalene-6,8-disulfonic acid was obtained as long slender needles; it crystallized with 2.5 moles of water. Very readily soluble in cold water (~ 1:1).

Found %: H_2O 9.62 (at 110-115°); K 17.75. $C_{10}H_5Cl(SO_3K)_2 \cdot 2.5\ H_2O$. Calculated %: H_2O 10.15; K 17.62.
For the substance dried at 110-115°, found %: K 19.65. $C_{10}H_5Cl(SO_3K)_2$. Calculated %: K 19.61.

The barium salt of 2-chloronaphthalene-6,8-disulfonic acid was obtained as long slender needles. It crystallizes with three moles of water; the substance loses one mole of water at 50-60°, the second at 120-130°, while the third molecule cannot be removed even at 230° (the substance decomposes).

Found %: H_2O 7.17 (at 120-130°); Ba 26.76. $C_{10}H_5Cl(SO_3)_2Ba \cdot 3H_2O$. Calculated %: (with $2H_2O$)H_2O 7.04; Ba 26.83.
For the substance dried at 120-130°, found %: Ba 28.86. $C_{10}H_5Cl(SO_3)_2Ba \cdot H_2O$. Calculated %: Ba 28.86

The calcium salt of 2-chloronaphthalene-6,8-disulfonic acid was obtained as long slender needles. It crystallizes with 5.5 moles of water; the substance loses two molecules of water at 60-70°, two at 110-115°, while the last 1.5 molecules cannot be removed even at 200° (the substance decomposes).

Found %: H_2O 16.01 (at 110-115°); Ca 8.73. $C_{10}H_5Cl(SO_3)Ca \cdot 5.5H_2O$. Calculated %: (with $4H_2O$) H_2O 15.67; Ca 8.72.
For the substance dried at 110-115°, found %: Ca 10.37. $C_{10}H_5Cl(SO_3)_2Ca \cdot 1.5H_2O$. Calculated %: Ca 10.34.

SUMMARY

1. The stepwise sulfonation of 2-chloronaphthalene with sulfuric acid monohydrate at 20° and with 19% oleum at 0° gives mainly 2-chloronaphthalene-6,8-disulfonic acid and a small amount of 2-chloronaphthalene-5,7-disulfonic acid.

2. The stepwise sulfonation of 2-chloronaphthalene with the monohydrate at 160° and with 19% oleum at 20° gives only 2-chloronaphthalene-6,8-disulfonic acid.

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HYDROLYSIS OF AROMATIC SULFONIC ACID ESTERS

II. INFLUENCE OF SUBSTITUENTS IN THE BENZENE RING ON THE HYDROLYSIS RATE OF ETHYL SULFONATES AND OF AROMATIC SULFONYL CHLORIDES

R. V. Visgert and E. K. Savchuk

The esters of aromatic sulfonic acids find use as alkylating agents in the alkylation of alcohols, phenols, mercaptans, thiophenols, etc. [1]. Their alkylating influence indicates rupture of the oxygen-alkyl radical bond in accord with the scheme:

$$C_6H_5SO_2{-}O{-}R + Y^- \rightarrow C_6H_5SO_2{-}O^- + RY,$$

where: R is an alkyl group, and Y^- is a nucleophilic reagent.

The reduction of alkyl sulfonates with lithium and aluminum hydrides leads to the formation of hydrocarbons, which also indicates rupture of the alkyl-oxygen bond [2]. Finally, the most trustworthy confirmation of the scheme given above is the hydrolysis of alkyl sulfonates with water, enriched with heavy oxygen [3,4], where again it is the O–C bond that cleaves, and not the S–O.

As a result, the mechanism for the hydrolysis of carboxylic acid and sulfonic acid esters is different: in the first case rupture of the acyl-alcohol oxygen bond occurs (acylating influence) [5], while in the second case the ester oxygen is from the side of the acid and it is the alkyl radical that cleaves (alkylating influence). The difference in the mechanism for the hydrolysis of sulfonic acid and carboxylic acid esters should be explained as being due to the molecular structural properties of each of the indicated compounds and above all, as being due to the influence shown by the nature of the radicals R and R_1 of the acid and alcohol components.

It seemed of interest to study the influence shown by the nature of electrophilic and nucleophilic substituents in benzenesulfonic acid on the hydrolysis rate of alkyl sulfonates. Such a study could be a convenient way of characterizing the properties and structural peculiarities of these substances. Literature data on a study of the hydrolysis rates of alkyl sulfonates exist only for several esters of ethyl alcohol [7-10].

The halides of aromatic sulfonic acids, from which the corresponding esters are directly obtained, are also an interesting study subject from the viewpoint of the manner in which the influence of substituents is transferred through the benzene ring to the sulfonyl chloride group. The kinetics for the hydrolysis of aromatic sulfonyl chlorides has been inadequately studied [11-14]. From the literature it is known that the aromatic sulfonyl halides are considerably less stable to water and alkalies than are the carboxylic acid halides [15]. It was established by V. G. Mairanovsky and M. V. Neiman [16] that the hydrolysis rate of sulfonyl chlorides is constant at pH 1–9, but further increase in the medium pH leads to a sharp increase in the hydrolysis rate. By studying the hydrolysis of aromatic sulfonyl halides and comparing it with the hydrolysis of the corresponding esters, we could not only judge as to their reactivity, which is of practical importance, but we could also follow the influence of the same substituents in the benzene ring on various active reaction centers (the sulfur of the sulfonyl chloride group in sulfonyl chlorides and the carbon of the alcohol radical in alkyl sulfonates).

The purpose of the present investigation was to study the influence of electrophilic and nucleophilic substituents on the hydrolysis rate of aromatic sulfonyl chlorides and the ethyl esters of substituted benzenesulfonic acids.

EXPERIMENTAL

As study subjects we took the substituted ethyl sulfonates and benzenesulfonyl chlorides, containing as substituents the groups: p-Cl, p-Br, p-NO_2, m-NO_2, o-NO_2, p-CH_3, p-CH_3O, p-CH_3CONH, 2,5-Cl_2, 3,5-$(NO_2)_2$.

The benzenesulfonyl chloride, p-toluenesulfonyl chloride, p-methoxybenzenesulfonyl chloride, m-nitrobenzenesulfonyl chloride and p-acetanilidesulfonyl chloride were obtained by reacting the corresponding substituted benzene with chlorosulfonic acid; the p-chlorobenzenesulfonyl chloride and p-bromobenzenesulfonyl chloride were obtained by reacting the sodium salts of the sulfonic acids with PCl_5. The o-nitrobenzenesulfonyl chloride was obtained from o-nitrochlorobenzene through o-dinitrodiphenyl disulfide by oxidizing the latter with chlorine in nitric acid [17]. 3,5-Dinitrobenzenesulfonyl chloride was obtained by sulfonating m-dinitrobenzene with oleum in the presence of mercury catalyst at 170-180°. The dinitrobenzenesulfonic acid was converted into the sulfonyl chloride through the calcium salt and subsequently treated with PCL_5 [18]. B. G. Boldyreva and B. Yu. Gordinsky were kind enough to supply us with the p-nitrobenzenesulfonyl chloride. The melting points of the sulfonyl chlorides and their chlorine analyses are given in Table 1.

TABLE 1

Constants of Substituted Benzenesulfonyl Chlorides

Value of X in the formula $XC_6H_4SO_2Cl$	Melting point	Chlorine analysis (in %)	
		found	calculated
H	*	20.43	20.11
4-Cl	52.5—53°	17.11	16.82
4-Br	76—77	14.24	13.89
4-CH_3	68—69	18.85	18.63
4-CH_3O	42—43	17.15	17.19
4-NO_2	79.5—80.5	15.85	16.02
3-NO_2	63—64	15.99	16.02
2-NO_2	68.5—69.5	15.90	16.02
4-CH_3CONH	149	15.43	15.20
3,5-$(NO_2)_2$	98—99	13.64	13.32
2,5-$(Cl)_2$	36—38	14.58	14.46

* M.p. 118-120°

TABLE 2

Constants of Substituted Ethyl Sulfonates

Value of X in the formula $XC_6H_5CO_2OC_2H_5$	Melting point
H	**
4-Cl	25°
4-Br	39—40
4-NO_2	91—92
4-CH_3	32—33
4-CH_3O	***
3-NO_2	42
2-NO_2	****
3,5-$(NO_2)_2$	92—93
2,5-$(Cl)_2$	74

** M.p. 130-131° (5 mm). *** M.p. 172-173° (5 mm). **** M.p. 158-160° (1 mm).

The substituted ethyl sulfonates were obtained by reacting the sulfonyl chlorides with an equimolar amount of sodium ethylate in either alcohol or alcohol-ether solution under suitable conditions. The constants of the ethyl sulfonates are given in Table 2.

The hydrolysis was run in 70% (by volume) aqueous dioxane medium [19]. The sulfonyl chlorides were hydrolyzed with water, and the ethyl esters of the benzenesulfonic acids, with the exception of the m-nitrobenzenesulfonic acid ester, were hydrolyzed with alkali. The m-nitrobenzenesulfonic acid ester was hydrolyzed with both alkali and water.

The method used to study the hydrolysis rate of the esters has been described in a previous communication [10]. In the present study we used a vessel with a side tube for the saponifications. This side tube was used to add the weighed specimen. Heated aqueous dioxane solution was introduced into the expanded portion of the flask up to the mark. The vessel was capped, placed in a thermostat, and kept for some time at the experimental temperature, after which the reagents were stirred rapidly, and the time when reaction started was noted. The saponification of the esters was run at 30, 50, and in some cases at 70°. The saponification of the sulfonyl chlorides was run at 30, 50, and in some cases at 0 and 15°. The size of the sulfonyl chloride and ester samples was again controlled by the final consumption of alkali, used to titrate the liberated acid. The concentration of the ethyl sulfonates and sulfonyl chlorides was of the order of 0.01 mole/liter; the KOH concentration was 0.033-0.035 mole/liter.

The rate constants for the hydrolysis of the aromatic sulfonyl chlorides and the aqueous hydrolysis of the esters were calculated by the equation for monomolecular reaction. The rate constants for the alkaline hydrolysis of the ethyl sulfonates were calculated by the equation for bimolecular reaction. The results of the experiments on the hydrolysis of aromatic sulfonyl chlorides and ethyl sulfonates are given in Tables 3 and 4. For comparison convenience the rate constants were recalculated to the dimensions liter/mole · second by the method of multiplying the constants, expressed in 1/ml · min, by a correction factor [19]. The energy of activation was calculated with the aid of the derived Arrhenius equation:

$$E=\frac{(\log k_2-\log k_1)\cdot 4.575\cdot T_1\cdot T_2}{T_2-T_1}.$$

The pre-exponential factor was obtained by taking the logarithm of the equation: $k = Pz \cdot e^{-E/RT}$.

TABLE 3

Influence of the Nature of Substituents in the Benzene Ring on the Hydrolysis Rate of Aromatic Sulfonyl Chlorides

Value of X	$k_{50} \cdot 10^5$	$k_{30} \cdot 10^5$	$k_{15} \cdot 10^3$ •	E(cal/mole)	log Pz (1/sec)
4-CH_3O	22.6	5.0	—	14550	6.20
4-CH_3	24.5	5.9	—	13810	5.74
4-CH_3CONH	28.75	7.7	—	13030	5.29
H	34.3	8.67	—	13430	5.63
2,5-$(Cl)_2$	34.17	9.1	—	12870	5.25
4-Br	49.1	13.8	—	12310	5.02
4-Cl	49.7	14.0	—	12310	5.03
2-NO_2	45.3	12.4	—	13580	5.87
3-NO_2	128.7	41.3	—	11000	4.55
4-NO_2	—	123.3	50.0	10350	4.56
3,5-$(NO_2)_2$	—	••	175.0	9110	3.93

• The rate constants have the dimensions 1/sec.

••Value of $k_0 \cdot 10^5 = 73.3$

TABLE 4

Influence of Substituents in the Benzene Ring on the Alkaline Hydrolysis Rate of Ethyl Sulfonates

Value of x	$k_{30} \cdot 10^3$	$k_{50} \cdot 10^3$	$k_{70} \cdot 10^3$ •••	E(cal/mole)	log Pz (liter/mole · sec)
4-CH_3O	—	0.248	1.655	20880	10.49
4-CH_3	—	0.291	1.815	20150	10.10
H	—	0.569	3.210	19070	9.65
4-Cl	0.210	1.445	—	18800	9.88
4-Br	0.220	1.440	—	18270	9.52
4-NO_2	1.0	6.52	—	17710	9.80
3-NO_2 ••••	0.833	3.45	—	18270	10.10
2-NO_2	2.08	14.08	—	18580	10.72
3,5-$(NO_2)_2$	•••••	—	—	—	—
2,5-$(Cl)_2$	0.906	5.925	—	18240	10.12

•••The rate constants have the dimensions liter/mole · sec.

••••For aqueous hydrolysis $k_{30} = 0.42 \cdot 10^{-3}$ and $k_{50} = 3.14 \cdot 10^{-3}$ 1/min.

•••••Value of $k_{15} = 1 \cdot 10^{-3}$.

DISCUSSION OF RESULTS

It is expedient to examine the data of the experimental results in three directions: 1) the influence of the substituent nature, 2) the influence of the substituent position in the ring, and 3) the cumulative influence of the same groups on the hydrolysis rate.

1. Based on their influence on the hydrolysis rate the substituents can be arranged in the following order:

$$4\text{-NO}_2 > 4\text{-Cl} > 4\text{-Br} > \text{H} > 4\text{-CH}_3\text{CONH} > 4\text{-CH}_3 > 4\text{-CH}_3\text{O}.$$

The electronegative groups increase, and the electropositive groups decrease the hydrolysis rate. The same sequence in the order of influence shown by substituents also holds in the alcoholysis of sulfonyl chlorides and aromatic sulfonic acid esters, which becomes evident when our data are compared with the literature data [9,20].

2. Nitro groups in different positions of the benzene ring exert a variable influence on the hydrolytic stability of the sulfonyl chlorides and ethyl esters of substituted benzenesulfonic acids. In their influence on the hydrolysis rate of sulfonyl chlorides the nitro groups can be arranged in the following order:

$$p\text{-NO}_2 > m\text{-NO}_2 > o\text{-NO}_2 > \text{H}.$$

A nitro group in the para position to the sulfonyl chloride group increases the hydrolysis rate by a factor of 3 when compared with the same group in the meta position; the saponification rate of the o-nitrobenzenesulfonyl chloride is $^1/_3$ that of the m-nitrobenzenesulfonyl chloride.

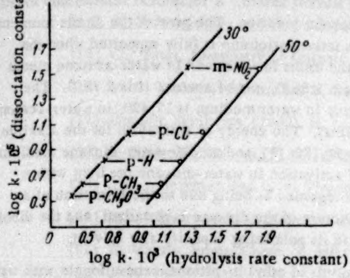
A completely different order in the influence shown by the position of the nitro group is observed for the corresponding nitrobenzenesulfonic acid ethyl esters:

$$o\text{-NO}_2 > p\text{-NO} > m\text{-NO}_2 > \text{H}.$$

The ethyl ester of o-nitrobenzenesulfonic acid is saponified at a rate that is 3 times that of the corresponding meta derivative, and approximately 30 times more rapidly than is the ester of the unsubstituted benzenesulfonic acid. Such a sharp difference in the influence shown by an o-NO_2 group on the hydrolysis rate of the sulfonyl chlorides and corresponding esters can, in our opinion, be explained by a difference in their hydrolysis mechanism. If the o-NO_2 group in the sulfonyl chlorides shows steric hindrance or the ortho-effect of the field appears [21], which, due to its close proximity to the active center, exerts a retarding influence on the hydrolysis rate, then in the sulfonic acid esters the sulfur is not such an active center, around which hydrolysis is initiated, and consequently substituents in the ortho position, showing a conjugation effect, do not exert steric hindrance, and as a result a strong increase in the saponification constants is observed for the o-nitro substituted sulfonic acid esters.

3. A symmetrical position of two nitro groups considerably increases the hydrolysis rate of both the benzenesulfonyl chloride and ethyl sulfonate (3,5-dinitrobenzenesulfonyl chloride and the corresponding ester are saponified very rapidly, and our experiments with them were run at 0 and 15° for the sulfonyl chloride and at 15° for the ester). A different situation is observed for the 2,5-dichloro-substituted benzenesulfonyl chloride and corresponding ester. Whereas the 2,5-dichlorobenzenesulfonyl chloride is saponified at nearly the same rate as benzenesulfonyl chloride, the corresponding chloro-substituted ester shows a saponification rate that is nearly 10 times that of the ethyl ester of the unsubstituted benzenesulfonic acid. Apparently, the difference in the rates is conditioned by the dissimilar influence shown by the chlorine in the ortho position to the sulfonyl chloride and sulfonic ester group on the hydrolysis rate. If in the sulfonyl chlorides, the presence of a substituent in the ortho position exerts a hindering effect, then in the corresponding ethyl alcohol esters an electrophilic substituent exerts an accelerating influence on the hydrolysis rate.

The experimental results reveal that linear relationships exist between the influence of substituents on the hydrolysis rate of aromatic sulfonyl chlorides and the influence of these same substituents on the value of the dissociation constants of the corresponding substituted benzoic acids (see figure). The detailed study of Hammett [22] indicates the linear character of the relationships existing between the rate constants of various reactions and the dissociation constants of all of the meta- and para-substituted benzoic acids. In the figure the logarithms of the dissociation constants of a number of substituted benzoic acids are plotted along the ordinate, while along the abscissa the logarithms of the hydrolysis rate constants of the corresponding aromatic sulfonyl chlorides are plotted. Both straight lines show satisfactory linear relationships, thus confirming the Hammett equation: $\log k - \log k_0 = \rho\sigma$, where: k is the hydrolysis rate constant of the sulfonyl chloride, k_0 is the dissociation constant of the corresponding substituted benzoic acid, σ is the constant of the substituent, depending only on its nature, and ρ is the reaction constant, characterizing a series of reactions and not depending on the nature of the substituent. From the graph it follows that the value of ρ for both reactions is the same, and the constant of the substituent σ is determined from the ratio $\sigma = \log \frac{k}{k_0}$.

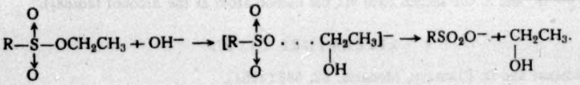


Linear relationships between the values of the hydrolysis constants of sulfonyl chlorides and the dissociation constants of the corresponding substituted benzoic acids. Explanation in text.

The results obtained in the kinetics studies support the postulation that in the hydrolysis of aromatic sulfonyl chlorides it is the sulfur of the sulfonyl chloride group that functions as the active reaction center, and the mechanism proposed by Hedlund [13] for the hydrolysis of sulfonyl chlorides with water (through dissociation of the sulfonyl chloride into ions) is not applicable to the hydrolysis of sulfonyl chlorides in aqueous dioxane medium.

Of the two factors, determining the hydrolysis rate of sulfonyl chlorides – the stability of the S–Cl bond and reaction with the solvent – the greatest importance in the given case is apparently possessed by the second. Although the introduction of electronegative substituents does increase the stability of the S–Cl bond, at the same time an increase in the positive charge on the sulfur facilitates approach of the water and solvent (formation of an intermediate complex) with subsequent addition of OH^- and simultaneous cleavage of HCl. Consequently, the introduction of electronegative substituents increases the hydrolysis rate of aromatic sulfonyl chlorides.

For the esters of aromatic sulfonic acids the obtained kinetics data – the presence of aqueous hydrolysis, and the influence of the nature and position of substituents on the hydrolysis rate – support the earlier proposed hydrolysis scheme with rupture of the bond at the alkyl radical [3,9]:



$$R-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-OCH_2CH_3 + OH^- \longrightarrow [R-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}O\ .\ .\ .\ \underset{\underset{OH}{|}}{CH_2}CH_3]^- \longrightarrow RSO_2O^- + \underset{\underset{OH}{|}}{CH_2}CH_3.$$

In contrast to the carbon of the carboxyl group, the sulfur in the esters of sulfonic acids is not the same active center around which the hydrolysis reaction is initiated. The difference in the hydrolysis mechanism of alkyl sulfonates and carboxylic acid esters is conditioned by the sharply electronegative properties shown by the benzenesulfonic acids, and in general preferential rupture of the RSO_2O-H bond could be expected for esters of strong acids, which is in agreement with the usual scheme for the electrolytic dissociation of acids [6]. Removal of electrons due to attraction along the chain creates a weak positive charge on the carbon atom of the alcohol radical, as a result of which the hydroxyl ion attacks it. Consequently, in alkyl sulfonates, the active reaction center will be the carbon atom of the alcohol radical. A parallelism in the influence of the same substituents on the hydrolysis of ethyl sulfonates and substituted benzenesulfonyl chlorides is due to the influence shown by substituents on the electrophilicity of the sulfur in the sulfonyl chloride group and the carbon atom of the alcohol radical in the esters.

The decisive factor in changing the reaction rate is to change the energy of activation. A change in the pre-exponential factor proceeds parallel with a change in the energy of activation. The values obtained by us for the pre-exponential factor and the energy of activation, both for the sulfonyl chlorides and for the ethyl sulfonates, are lower than those given in the studies of Hedlund [13] (for water), N. V. Sapozhnikova and Z. G. Linetskaya [14], and also Tommila [12] (for a 56% water-acetone mixture). A reduction in the energy of activation can be regarded as being due to the influence of the solvent nature. A reciprocal relationship exists between the value of the hydrolysis activation energy and the solvent polarity. The greater the dipole moment of the solvent, the lower the hydrolysis activation energy. This interrelationship is fully supported when the activation energies for the hydrolysis of the sulfonyl chlorides and esters in water and in water-acetone media are compared (data of Hedlund). The dipole moment of water is 1.85 D, and of acetone it is 2.72 D. The energy of activation for the hydrolysis of benzenesulfonyl chloride in water medium is 17,420; in water-acetone it is 14,430; and in water-dioxane it is 13,430 cal/mole (our data). The energy of activation for the alkaline hydrolysis of the ethyl ester of benzenesulfonic acid in water is 21,120 [9], and in 70% water-dioxane medium it is 19,070 cal/mole (our data). A reduction in the energy of activation in water-dioxane medium with a small dipole moment for the dioxane (0.4 D) can apparently be regarded as being due to the formation of an intermediate complex, as a result of which the symmetrical structure of the dioxane is disturbed, and the dipole moment of the molecule increases, which leads to an increase in its polarizing capacity as a solvent.

The close values of the energy of activation for the hydrolysis of ethyl m-nitrobenzenesulfonate with water (E = 19,570) and with alkali (E = 18,270) indicates that the main reaction, determining the energy of activation, is the addition of the OH^- ion to the carbon of the alcohol radical. Although the constant for the dissociation of water into ions is small, still the energy of activation for this process is considerably less than the energy of activation for the addition of OH^- ions, and consequently the latter determines the rate of the hydrolysis reaction.

SUMMARY

1. We studied the hydrolysis rate of 11 substituted aromatic sulfonyl chlorides and 10 ethyl esters of substituted benzenesulfonic acids. Here we established the influence of the nature, position and accumulation of the same groups in the benzene ring on the hydrolysis rate.

2. Substituents in the para position of the benzene ring exert the same type of influence on the hydrolysis rate of both the sulfonyl chloride and sulfonic ester bond. When compared with either meta or para substituents, substituents in the ortho position decrease the hydrolysis rate of sulfonyl chlorides and increase the hydrolysis rate of the corresponding ethyl esters.

3. Linear relationships exist between the influence of substituents on the hydrolysis rate of aromatic sulfonyl chlorides and the influence of these same substituents on the dissociation constants of the corresponding acids.

4. Our experimental data support the postulation that the hydrolysis of aromatic sulfonyl chlorides and of the corresponding esters is accomplished through different active centers (in the first case via the sulfur of the sulfonyl chloride group, and in the second case via the carbon atom of the alcohol radical).

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HYDROLYSIS OF AROMATIC SULFONIC ACID ESTERS

III. HYDROLYSIS OF PHENYL ESTERS OF SUBSTITUTED BENZENESULFONIC ACIDS

R. V. Vizgert and E. K. Savchuk

No attempt has been made to study the kinetics for the hydrolysis of the esters of phenol with aromatic sulfonic acids. In a previous communication [1] on a study made of the influence shown by the nature of alcohol components with different acidity (ethyl alcohol, phenol, 4,4'-dihydroxydiphenyl sulfone, 4-hydroxydiphenyl sulfone) on the hydrolysis rate of benzenesulfonic acid esters it was mentioned that the esters of phenol, in contrast to the esters with other alcohol components, are saponified at a slower rate. The parallelism established earlier for carboxylic acid esters [2] between the acid properties of the alcohol components and the hydrolysis rate is disturbed for the esters of phenol with a benzenesulfonic acid.

In their influence on the hydrolysis rate of benzenesulfonic acid esters the alcohol components can be arranged in the following order:

$$C_6H_5OH < C_2H_5OH < 4{,}4'\text{-}HOC_6H_4SO_2C_6H_4ONa < 4\text{-}HOC_6H_4SO_2C_6H_5.$$

The purpose of the present investigation was to study the influence shown by electrophilic and nucleophilic substituents in the benzene ring of sulfonic acids on the hydrolysis rate of the phenyl esters of benzenesulfonic acids, and to compare the obtained data with the influence shown by the same substituents on the hydrolysis rate of ethyl sulfonates.

EXPERIMENTAL

As study subjects we took the esters of phenol with substituted benzenesulfonic acids, the latter containing as substituents the groups: p-Cl, p-Br, p-NO_2, m-NO_2, o-NO_2, p-CH_3, p-CH_3O, 2,5-$(Cl)_2$, 3,5-$(NO_2)_2$.

The esters were prepared by reacting substituted benzenesulfonyl chlorides with sodium phenolate in anhydrous alcohol, with subsequent isolation and recrystallization [3]. The melting points of the obtained phenyl esters of benzenesulfonic acids are given in Table 1.

The hydrolyses were run in a 70% water-dioxane medium of alkali. The hydrolysis rate was determined by titration of the formed acids with alkali in the presence of Methyl Red indication. The saponification was run at 30, 50, and in some cases at 70°. The method of running the experiments has been described by us earlier [1,2]. The initial concentration of the esters was 0.012 mole/liter, and of the KOH it was 0.033-0.035 mole/liter.

In contrast to the corresponding ethyl esters, the phenyl esters of benzenesulfonic acids are not hydrolyzed by water. Prolonged saponification of the phenyl ester of p-chlorobenzenesulfonic acid with water at 70° for 10 days, followed by heating at the boil, did not produce any changes. The hydrolysis of the esters is accomplished by the equation:

$$C_6H_5OSO_2C_6H_4X + 2KOH \rightarrow C_6H_5OK + XC_6H_4SO_2OK + H_2O.$$

TABLE 1

Melting Points of Phenyl Esters ($XC_6H_4SO_2OC_6H_5$)

Value of	Melting point
H	35—36°
4-Cl	92—93
4-Br	115—116
$4-CH_3$	94—95
$4-CH_3O$	56—57
$4-NO_2$	113—114
$3-NO_2$	94
$2-NO_2$	57
$3,5-(NO_2)_2$	101
$2,5-(Cl)_2$	91—92

The hydrolysis rate constants were calculated with the aid of the 2nd order equation, taking into consideration a double consumption of alkali:

$$\frac{dx}{dt} = k(a-2x)\cdot(b-x),$$

where a is the alkali concentration, and b is the ester concentration. The energy of activation was calculated with the aid of the derived Arrhenius equation:

$$E = \frac{(\log k_2 - \log k_1)\cdot 4.575\cdot T_1\cdot T_2}{(T_2-T_1)}.$$

The results of the experiments on the hydrolysis of aryl sulfonates are given in Table 2. In this table the constants are recalculated to the dimensions liter/mole · sec by the method of multiplying the earlier obtained constants by the correction factor V/N · 60, where N is the normality of the alkali used for titration, and V is the volume of the specimen (in ml).

TABLE 2

Influence of the Nature of Substituents in the Benzene Ring of Sulfonic Acids on the Hydrolysis Rate of Aryl Sulfonates When Compared with Alkyl Sulfonates

Value of X	Aryl sulfonates $XC_6H_4SO_2OC_6H_5$					Ethylsulfonates $XC_6H_4SO_2OC_2H_5$		
	$k_{30}\cdot 10^3$	$k_{50}\cdot 10^3$	$k_{70}\cdot 10^3$	E (cal/mole)	$\log P_z$ (liter/mole · sec)	$k_{30}\cdot 10^3$	E (cal/mole)	$\log P_z$ (liter/mole · sec)
$4-CH_3O$	—	0.076	0.437	19260	8.92	0.248	20880	10.49
$4-CH_3$	—	0.145	0.790	18650	8.78	0.291	20150	10.10
H	0.059	0.374	1.897	17860	8.66	0.569	19070	9.65
4-Cl	0.191	1.120	—	17190	8.72	1.445	18800	9.88
4-Br	0.195	1.128	—	17060	8.60	1.440	18270	9.52
$4-NO_2$	6.79	26.3	—	13160	7.40	6.52	17710	9.80
$3-NO_2$	2.40	11.44	—	15200	8.35	5.45	18270	10.10
$2-NO_2$	1.35	7.34	—	16340	8.92	14.08	18580	10.72
$3,5-(NO_2)_2$	*	—	—	—	—	**	—	—
$2,5-Cl_2$	0.516	2.97	—	17030	9.00	5.92	18240	10.12

* $k_{15}\cdot 10^3 = 5.8$. ** $k_{15}\cdot 10^3 = 1.0$.

DISCUSSION OF RESULTS

The influence of the nature of substituents in the benzene ring of sulfonic acids on the hydrolysis of aryl sulfonates and of ethyl sulfonates is unitypical in direction. The electrophilic substituents – NO_2, Cl, Br – increase, and the electron-donor substituents – CH_3, CH_3O – decrease the hydrolysis rate (Table 2). The same sequence in the influence of substituents is also observed in the hydrolysis of aromatic sulfonyl chlorides [4] and of carboxylic acid esters [5].

If the sequence of the influence shown by various substituents on the hydrolysis rates of the ethyl and aryl sulfonates is the same, then the relative magnitude of the influence shown by each of these substituents on the rates of the two reactions is different (Table 2). The phenyl benzenesulfonate is saponified at a slower rate than is the corresponding ethyl ester. The hydrolysis rates of the esters with the two alcohol components are made somewhat more equal by the introduction of either a chlorine or bromine atom in the para position. The hydrolysis rate of the ethyl ester is reduced by a factor of 2.3 when the p-methoxy group is introduced, while that of the phenyl ester is reduced by a factor of 5. With the introduction of a nitro group in the meta , and especially in the para position, the hydrolysis rates of the phenyl esters begin to exceed the hydrolysis rates of the ethyl esters (the introduction of a NO_2 group in the para position increases the hydrolysis rate of the ethyl ester by a factor of 11.5, and that of the phenyl ester by a factor of 70). When the 3,5-dinitro group is introduced the saponification rate of the phenyl ester is 6 times that of the corresponding ethyl ester. This data shows that substituents in the acid component exert a greater influence on the hydrolysis rates of phenyl esters than they do on ethyl esters.

The above postulation is supported by a change in the energy of activation and of the pre-exponential factor. The energy of activstion and the pre-exponential factor are lower for the phenyl esters than for the ethyl esters, and show greater variation. The lowest energy of activation and pre-exponential factor in the case of the p-nitro derivatives are,- for the aryl sulfonates 13,160 and 7.4, respectively, and for the ethyl sulfonates, 17,710 and 9.8. The highest values are observed in the case of the methoxy derivatives - for the aryl sulfonates, 19,260 and 8.92, and for the ethyl sulfonates, 20,880 and 10.49. The wide variations in the values of the energy of activation and of the pre-exponential factor for the aryl sulfonates are due to the greater influence exerted by the nature of the substituents in the acid component on the hydrolysis rates of the aryl sulfonates when compared with the ethyl sulfonates.

The variable influence shown by the positions of substituents on the hydrolysis rates of the ethyl and aryl sulfonates appears with especial clarity when substituents are introduced in the ortho position. The saponification rate of the ethyl ester of o-nitrobenzenesulfonic acid is twice that of the corresponding p-nitrobenzenesulfonic acid ester, while the saponification rate of the phenyl ester of o-nitrobenzenesulfonic acid is $^1/_4$ that of the corresponding p-nitrobenzenesulfonic acid ester. Based on their influence on the hydrolysis rate, the nitro groups can be arranged in the following order:

for the esters of ethyl alcohol $o\text{-}NO_2 > p\text{-}NO_2 > m\text{-}NO_2 > H$,
for the esters of phenol $p\text{-}NO_2 > m\text{-}NO_2 > o\text{-}NO_2 > H$.

The esters of the 2,5-dichlorobenzenesulfonic acids are saponified more rapidly than are the corresponding unsubstituted esters, in which connection the increase in hydrolysis rate is especially pronounced for the ethyl ester, and here the saponification rate of the ethyl ester of 2,5-dichlorobenzenesulfonic acid is twice that of the corresponding phenyl ester. As a result, the introduction of substituents in the ortho position (when compared with the meta and para positions) facilitates hydrolysis of the ethyl sulfonates and retards hydrolysis of the aryl sulfonates.

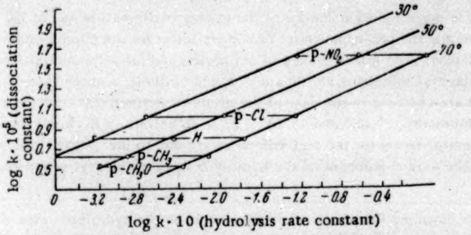
It is interesting to mention that the influence of substituents in the ortho position on the hydrolysis rates of aryl sulfonates is unitypical in direction with the influence shown by ortho substituents on the hydrolysis rates of aromatic sulfonyl chlorides and carboxylic acid esters, which is evident when the data in Table 3 are examined. The o-nitro derivatives of ethyl benzoate and of the aryl sulfonate are saponified more rapidly than are the unsubstituted esters, but at a considerably slower rate than the m-, and especially the p-nitro derivatives.

TABLE 3

Influence of the Position of the Nitro Group in the Benzene Ring on the Hydrolysis Rate of Aromatic Sulfonyl Chlorides, Aryl Sulfonates and the Ethyl Esters of Carboxylic Acids and Sulfonic Acids (Values $k_{50} \cdot 10^5$)

Substituent X	H	$m\text{-}NO_2$	$p\text{-}NO_2$	$o\text{-}NO_2$
$XC_6H_4SO_2Cl$	34.3	128.7	—	45.3
$XC_6H_4SO_2OC_6H_5$	37.4	1144.0	2630.0	734.0
$XC_6H_4CO_2C_2H_5$	55.0	3110.0	5090.0	334.0
$XC_6H_4SO_2OC_2H_5$	56.9	545.0	652.0	1408.0

Hammett gives the equation $\log k - \log k_0 = \rho\sigma$ for various reactions involving a substituted benzene ring. We calculated the reaction constants for the hydrolysis of aryl sulfonates as $\rho = 2.2$, and for the hydrolysis of benzenesulfonyl chlorides as $\rho = 0.93$. The value of 2.2 for the hydrolysis constant of aryl sulfonates is close to the value of 2.5, calculated by Hammett [7] for the hydrolysis constant of the ethyl benzoates. The linear character of the relationships between the dissociation constants of some benzoic acids and the hydrolysis constants of the corresponding aryl sulfonates is shown in the figure.



Linear relationships between the values of the hydrolysis constants of aryl sulfonates and the dissociation constants of the corresponding benzoic acids. Explanation in text.

On the basis of Hammett's equation we calculated the hydrolysis rate constants for the phenyl esters of substituted benzenesulfonic acids with p-NH_2, and various substituents in the meta position. The calculated values of the constants, together with the experimental data, taken from Table 2, are given in Table 4.

A similar order in the influence shown by meta- and para-substituents is also observed for the esters of carboxylic acids [8] (Table 5).

TABLE 4

Influence of the Position of Substituents in Benzenesulfonic Acids on the Hydrolysis Rate of Aryl Sulfonates ($k_{50} \cdot 10^3$ 1/ml · min)

Substituent X	p-$XC_6H_4SO_2OC_6H_5$	m-$XC_6H_4SO_2OC_6H_5$
NH_2	0.0027	0.034
CH_3O	0.015	0.142
CH_3	0.030	0.055
H	0.078	0.078
Cl	0.233	0.525
NO_2	5.50	2.27

TABLE 5

Influence of the Position of Substituents in Carboxylic Acid Esters on the Hydrolysis Rate ($k_{25} \cdot 10^3$)

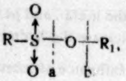
Substituent X	p-$XC_6H_4COOC_2H_5$	m-$XC_6H_4COOC_2H_5$
NH_2	1.1	20.0
CH_3O	11.0	59.0
CH_3	23.0	35.0
H	55.0	55.0
Cl	212.0	363.0
NO_2	5090.0	3110.0

Substituents of the 1st type in the meta position show a greater influence on the hydrolysis rate than when in the para position: m-XC_6H_4 > p-XC_6H_4. In reverse, substituents of the 2nd type in the para position show a greater influence on the hydrolysis rate than when in the meta position: p-XC_6H_4 > m-XC_6H_4.

As a result, the aryl sulfonates show a greater resemblance to the esters of carboxylic acids than they do to the ethyl sulfonates.

The experimental data obtained by us – the absence of hydrolysis under the influence of water, the greater influence of both electrophilic and nucleophilic substituents on the hydrolysis rate of phenyl esters when compared with the corresponding ethyl esters, the variable influence of substituents in the ortho position, and the analogy in the influence of the nature and position of substitutents on the hydrolysis rates of both aryl sulfonates and carboxylic acid esters – all permit expressing the postulation that the mechanism for the hydrolysis of the aryl sulfonates and alkyl sulfonates is different.

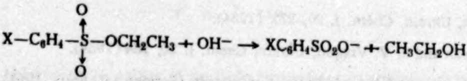
Of the two possible directions for the hydrolysis of sulfonic acid esters [9]:



$$R-\overset{O}{\overset{\uparrow}{\underset{\underset{O}{\downarrow}}{S}}}-O-R_1.$$

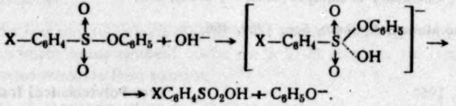
the most probable here is rupture of bond (*a*).

The hydrolysis of ethyl sulfonates is accompanied by rupture of the alkyl-oxygen bond (b) in accord with the scheme [6]:



$$X-C_6H_4-\overset{O}{\overset{\uparrow}{\underset{\underset{O}{\downarrow}}{S}}}-OCH_2CH_3 + OH^- \longrightarrow XC_6H_4SO_2O^- + CH_3CH_2OH.$$

In this case the active reaction center – the carbon of the alcohol radical – is removed from the substituent into the benzene ring, and consequently substituents in the acid component show but slight influence on the hydrolysis rate. For the phenyl esters, due to the difficulty of nucleophilic attack by the OH^- ion on the phenyl radical, hydrolysis apparently proceeds as the result of the OH^- ion attacking the sulfur atom, and requires a transitional state in accord with the probable scheme:



$$X-C_6H_4-\overset{O}{\overset{\uparrow}{\underset{\underset{O}{\downarrow}}{S}}}-OC_6H_5 + OH^- \longrightarrow \left[X-C_6H_4-\overset{O}{\overset{\uparrow}{\underset{\underset{O}{\downarrow}}{S}}}\begin{smallmatrix}OC_6H_5\\OH\end{smallmatrix}\right]^- \longrightarrow$$

$$\longrightarrow XC_6H_4SO_2OH + C_6H_5O^-.$$

The experiments of Kenner [10] on the reduction of alkyl and aryl sulfonates with lithium and aluminum hydrides also speak in favor of this scheme. The first are reduced to hydrocarbons, i.e. rupture is at the alkyl bond, while the second show rupture of the bond between sulfur and oxygen.

The difference in the hydrolysis mechanism of alkyl and aryl sulfonates, containing the same acid components, but different alcohol components, is conditioned by the nature of the latter.

The above hydrolysis scheme is in good agreement with the experimental data: for the aryl sulfonates a substituent in the benzene ring will be considerably closer to the active reaction center – the sulfur of the sulfo group, and consequently its influence on the hydrolysis rate constant, the energy of activation and the pre-exponential factor, will appear to a greater degree than for the case of the alkyl sulfonates. A shift of the active reaction center from the carbon of the alcohol radical (for the alkyl sulfonates) to the sulfur of the sulfo group (for the aryl sulfonates) is the reason for the different influence shown by substituents in the ortho position. Ortho substituents show a retarding influence on the hydrolysis rate of aryl sulfonates, aromatic sulfonyl chlorides and carboxylic acid esters, where the active reaction centers – the sulfur of the sulfo group and the carbon of the carboxyl group – are directly attached to the benzene ring, and accelerate the hydrolysis rate of the ethyl sulfonates, where the active reaction center is somewhat removed. In the first case the observed reduction in the hydrolysis rate is conditioned by the presence of the ortho effect, while in the second case the ortho effect is absent.

As a result, the experimental results obtained in studying the influence shown by the nature and position of substituents on the hydrolysis rates of alkyl and aryl sulfonates indicate that here the reaction mechanism is different.

SUMMARY

1. We studied the alkaline hydrolysis rate of 10 synthesized phenyl esters of substituted benzenesulfonic acids.

2. In contrast to the ethyl sulfonates, the corresponding phenyl esters are not hydrolyzed by water.

3. Substituents in the acid component show a greater influence on the hydrolysis rate of phenyl esters than on ethyl esters.

4. When compared with substituents in the meta- and para positions, substituents in the ortho-position reduce the hydrolysis rate of phenyl esters and increase the hydrolysis rate of ethyl esters.

5. A parallelism was established in the influence of substituents in the ortho-, meta- and para positions on the hydrolysis rate of aryl sulfonates and of ethyl benzoates.

6. A theory was expressed relative to a possible mechanism for the hydrolysis of aryl sulfonates, where the oxygen remains attached to the phenyl radical.

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Lvov Polytechnical Institute

PREPARATION OF 1-(2'-CHLORO-5'-SULFOPHENYL)-3-METHYL-5-PYRAZOLONE FROM THE AMIDE OF ACETOACETIC ACID

P. A. Levin

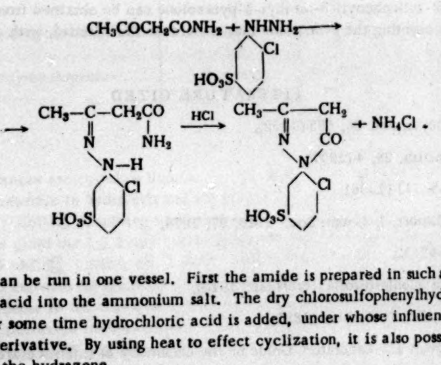
Claisen and Meyer [1] studied the ability of the hydrazones of acetoacetamide to be easily converted into pyrazolones. Formation of the pyrazolone ring proceeds in water medium when the hydrazone is acidified with mineral acid. Prior to the discovery of diketene, the amide of acetoacetic acid was obtained in very low yield [1-3], and its utilization for the synthesis of pyrazolones could not even be discussed. The use of diketene makes acetoacetamide, together with other acyl derivatives of acetoacetic acid, a readily available product.

The existing two methods [4,5] for the preparation of acetoacetamide from diketene possess essential limitations. The first is associated with the use of the ester and requires cooling to −10 to −15°. The second method does not take into sufficient consideration the influence of temperature and excess ammonia. A very large excess of ammonia leads to conversion of part of the acetoacetamide into the amide of aminocrotonic acid and products of further polymerization.

We established that the best way to aminate diketene is to charge it into 2% ammonia solution in a mixture of water and ice. Here the whole amide synthesis can be run in 20-30 minutes. For further operation it is unnecessary to isolate the acetoacetamide from solution.

If the extreme paucity of information given in Cohn's monograph [6] is neglected, where mention is made of 1-(2'-chloro-5'-sulfophenyl)-3-methyl-5-pyrazolone, then the preparation of the latter is not described in the literature.

The total synthesis of the chlorosulfophenylmethylpyrazolone can be depicted in the following manner:



The complete process can be run in one vessel. First the amide is prepared in such a manner that the ammonia converts the sulfonic acid into the ammonium salt. The dry chlorosulfophenylhydrazine is then added to the amide solution. After some time hydrochloric acid is added, under whose influence the hydrazone is converted into the pyrazolone derivative. By using heat to effect cyclization, it is also possible to considerably accelerate the step of forming the hydrazone.

EXPERIMENTAL

To a mixture of 50 ml of water, 50 g of ice and 13.5 ml of 18% ammonia in a beaker was added in 5 minutes with stirring 4.3 ml (0.05 mole) of diketene. The temperature of the reaction mixture was kept below 4°. The mixture was allowed to stand for 20 minutes, in which time the diketene had dissolved completely.

The 2-chlorosulfonphenylhydrazine was obtained in good yield from 2-nitrochlorobenzene by sulfonation, reduction to the amine, diazotization, and reduction of the diazo compound.

The existing methods [7] for the preparation of 2-chloro-5-sulfonitrobenzene suffer from a number of disadvantages (the use of 30% oleum or solid pyrosulfuric acid, the long duration of the syntheses, numerous extractions, evaporations, isolation through the barium salt, reduction with ferrous sulfate, etc.).

We were able to obtain the nitro compound and amine much more simply and in good yield. A mixture of 240 g of 2-nitrochlorobenzene with 5 weight parts of 7% oleum was heated on the water bath for 5 hours. The reaction mixture was poured over a small amount of ice; the precipitate of 2-chloro-5-nitrosulfobenzene was separated on a filter, and then neutralized with the calculated amount of 40% sodium hydroxide.

The nitro compound under heating and stirring was reduced with iron filings in dilute hydrochloric acid. The yield of 2-chlorometanilic acid was 88% (with an amine content of 93%), based on 2-nitrochlorobenzene. Conversion of the 2-chlorometanilic acid into the hydrazine was effected by the method used for the conversion of sulfanilic acid [8].

The 2-chloro-5-sulfophenylhydrazine isolated from the reaction mass was washed on the filter with ice water, pressed well, and recrystallized from hot water (solubility 20 g/liter).

The pure product is a light, grayish-rose, crystalline powder, containing 92-95% hydrazine (yield 70-75%); it decomposes when heated.

To 0.105 mole of the acetoacetamide solution was added with stirring 0.1 mole of dry chlorosulfophenylhydrazine. The mixture was kept at 18-20° for 1 hour, after which 33 ml of hydrochloric acid (d 1.14) was added. The cyclization process was run for 40 minutes at 55-60°. The mixture on cooling gave the 1-(2'-chloro-5'-sulfophenyl)-3-methyl-5-pyrazolone as yellow rhombic crystals (with 1 mole of H_2O), which were separated from the mother liquor, washed, and dried. Yield 92%.

SUMMARY

1. The amide of acetoacetic acid can be obtained in nearly quantitative yield by the amination of diketene with aqueous ammonia solutions (1.5-3%) in the presence of ice. The obtained acetoacetamide solutions can be used directly for the synthesis of pyrazolones.

2. 1-(2'-Chloro-5'-sulfophenyl)-3-methyl-5-pyrazolone can be obtained from the amide of acetoacetic acid in 92% yield (not counting the pyrazolone that remains in the filtrate), with a purity of 98-99% for the main reaction product.

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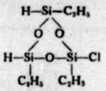
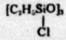
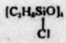
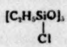
ORGANOCYCLOSILOXANES

II. ETHYLCHLOROCYCLOSILOXANES

N. N. Sokolov and S. M. Akimova

By chlorinating methylcyclosiloxanes of the type $(CH_3SiHO)_n$ (n = 4–7) we were able to obtain [1] methylchlorocyclosiloxanes of the type $(CH_3SiClO)_n$. It was found that the chlorination reaction could also be successfully used for the preparation of the ethylchlorocyclosiloxanes. The chlorination of the ethylcyclosiloxanes is less exothermic than is the corresponding reaction for the methylcyclosiloxanes, and consequently can be run without using carbon tetrachloride as a diluent for the reaction mixture. The compounds that we prepared and their basic properties are shown in Table 1.

TABLE 1

Compound	Formula	B.p. (pressure in mm)	M.p.	d_{20}^{20}
1,3,5-Triethyl-1-chlorocyclotrisiloxane		125° (20)	−65°	1.0876
1,3,5-Triethyl-1,3-dichlorocyclotrisiloxane	$[C_2H_5SiO]_3Cl_2H$	150—151 (20)	−60	1.1928
Tri-(ethylchloro)-cyclotrisiloxane	 $[C_2H_5SiO]_3$ with Cl: $[C_2H_5Si(Cl)O]_3$	126—127 (2)	−43	1.2591
Tetra-(ethylchloro)-cyclotetrasiloxane	 $[C_2H_5Si(Cl)O]_4$	163—165 (2)	−62	1.2745
Penta-(ethylchloro)-cyclopentasiloxane	 $[C_2H_5Si(Cl)O]_5$	187—190 (2)	−40	1.2988

All of the obtained substances are colorless liquids. As with other organochlorosilanes, the ethylchlorocyclosiloxanes are highly susceptible to hydrolysis and are gradually hydrolyzed even by moist air. When hydrolyzed under mild conditions (cooling, dissolving in diethyl ether) the monochlorinated triethylcyclotrisiloxane $(C_2H_5SiO)_3ClH_2$ gives in good yield the 1,3,5-triethyl-1-hydroxycyclotrisiloxane $(C_2H_5SiO)_3(OH)H_2$, m.p. 112-114° (2 mm), b.p. from −41 to −43°, d_{20}^{20} 1.0588, n_D^{20} 1.4288. This hydroxyl derivative is stable; it distills in vacuo almost without decomposition and does not condense to the dimer when hydrolyzed in either acid or slightly alkaline medium, but it does condense in the course of several minutes with dry hydrogen chloride at the hydroxyl groups. Hydrolysis of the dichlorinated triethylcyclotrisiloxane $(C_2H_5SiO)_3Cl_2H$ gave the 1,3,5-triethyl-1,3-dihydroxycyclotrisiloxane $(C_2H_5SiO)_3(OH)_2H$; b.p. −8°, d_{20}^{20} 1.1207, n_D^{20} 1.4345; this product turned to a gel when an attempt was made to vacuum-distill it. A characteristic of these two hydroxy derivatives is their solubility, not only in aromatic compounds (benzene, toluene), but also in the paraffin hydrocarbons (benzine, heptane, mineral spirits). An attempt to obtain the hydroxyl derivatives of the tri-, tetra- and penta-(ethylchloro)-cyclosiloxanes gave negative result: when hydrolyzed these substances give hard powderlike polymers.

The ethylchlorocyclosiloxanes show characteristic behavior with respect to the action of concentrated sulfuric acid. When treated with 1% sulfuric acid, the triethylcyclotrisiloxane is polymerized with ring cleavage in about 20 minutes; when one chlorine atom is introduced, the polymerization goes in 10 minutes, while polymerization does not take place when a hydrogen on the silicon atom is replaced by two or more chlorine atoms.

EXPERIMENTAL

Preparation of starting ethylcyclosiloxanes. Ethylcyclosiloxanes of the $[C_2H_5SiHO]_{3-5}$ type were obtained by the hydrolysis of ethyldichlorosilane $C_2H_5SiHCl_2$ (m.p. 74°, % Cl 54.92, % H, bound with Si, 0.75) with a mixture of water and ethyl alcohol; here the same result was obtained as in the earlier described method [2] of hydrolysis in diethyl ether medium, in which connection the process can be run without deep cooling of the reaction mixture. In a glass hydrolyzer with jacket for water cooling was placed 500 g of water and 250 g of alcohol, from a dropping funnel was added in 1 hour 200 g of $C_2H_5SiHCl_2$, while the average hydrolysis temperature was 17°. The hydrolysis product was deparated in a separatory funnel, diluted with a half volume of ether, washed, and the ether removed by vacuum-distillation. The residue analyzed 41% cyclic compounds (distilling up to 200°), which showed an ethoxyl content of 0.2% and an H content of 1.34% (linked with Si).

After combining the products of a number of experiments, the lower cyclic compounds were vacuum-distilled in a nitrogen stream, using a 10-theoretical plate column for their separation. The characteristics of the ethylcyclosiloxanes isolated in this manner are given in Table 2. Since these substances show association at the hydrogen bonds, their molecular weight in benzene was determined by the method of using different concentrations of substance and then graphically extrapolating to infinite dilution (the same is also true for the ethylhydroxycyclosiloxanes).

TABLE 2

Compound	B. p. at 20mm	d_{20}^{20}	n_D^{20}	*M* found	*M* calc.	Yield (in %)
Triethylcyclotrisiloxane *	105	0.9835	1.4153	223	222	48
Tetraethylcyclotetrasiloxane	136.2	0.9922	1.4178	296	296	33
Pentaethylcyclopentasiloxane	165.2	1.0012	1.4222	374	370	11

*Melting point 100°.

1,3,5-Triethyl-1-chlorocyclotrisiloxane. Individual portions of the triethylcyclotrisiloxane were chlorinated by the earlier described method [1] at 30-35° in such manner that the mono- and dichlorinated products were obtained (based on the increase in weight). After chlorination, 230 g of the chlorinated triethylcyclotrisiloxane was fractionally distilled through a 10-theoretical plate column at 20 mm. At 125° there was collected 55 g of 1,3,5-triethyl-1-chlorocyclotrisiloxane.

Found %: C 27.78; H 6.65; H(–Si) 0.78; Si 32.68; Cl 13.94. M 262. $C_6H_{17}Si_3O_3Cl$. Calculated %: C 28.07; H 6.62; H(–Si) 0.78; Si 32.74; Cl 13.84. M 256.5.

1,3,5-Triethyl-1,3-dichlorocyclotrisiloxane was isolated from the preceding distillation at 150-151° (20 mm) in an amount of 23 g.

Found %: C 23.80; H 5.27; H(–Si) 0.33; Si 28.54; Cl 24.56. M 298. $C_6H_{16}Si_3O_3Cl_2$. Calculated %: C 24.74; H 5.49; H(–Si) 0.34; Si 28.86; Cl 24.41. M 291.

The same product was also obtained by chlorinating 20 g of the triethylcyclotrisiloxane to the calculated weight of 26.2 g and subsequent distillation from a Wurtz flask at 20 mm. Three fractions were isolated: 1st, 136-144° (1 g); 2nd, 144-151° (8 g) (% Cl 24.46) and 3rd, 152-156° (10 g) (% Cl 23.98), still residue 6 g. This shows that chlorination of the ethylcyclosiloxanes proceeds quite smoothly and the obtained products show but slight deviations from the desired degree of chlorination.

Tri-(ethylchloro)-cyclotrisiloxane. Twenty grams of triethylcyclotrisiloxane was chlorinated at 30-35° in 40 minutes to a weight increase of 9.7 g (required by theory 9.3 g). Distillation from a Wurtz flask at 2 mm gave a fairly homogeneous product; 5 g at 120-123° (% Cl 31.40), 7 g at 124-125° (% Cl 31.63) and 7 g at 126-127°. The last fraction was analyzed.

Found %: C 22.88; H 4.56; Si 25.93; Cl 32.30. M 330. $C_6H_{15}Si_3O_3Cl_3$. Calculated %: C 22.11; H 4.60; Si 25.80; Cl 32.71. M 325.5

Tetra-(ethylchloro)-cyclotetrasiloxane. Twenty grams of tetraethylcyclotetrasiloxane was chlorinated in 45 minutes to a weight of 30 g (0.5 g in excess of theory), and the product was distilled from a Wurtz flask at 2 mm into 3 fractions with b.p. from 158 to 170°. The 163-165° fraction, weighing 8 g, was analyzed.

Found %: C 21.82; H 4.58; Si 25.81; Cl 32.28. M 455. $C_8H_{20}Si_4O_4Cl_4$. Calculated %: C 22.11; H 4.60; Si 25.80; Cl 32.71. M 434.

Penta-(ethylchloro)-cyclopentasiloxane. Here 9.5 g of the pentaethylcyclopentasiloxane was chlorinated to a weight increase slightly in excess of theory (13.8 g), and the chlorination product was distilled from a Wurtz flask at 2 mm. The fraction with b.p. 187-190° was collected (6 g).

Found %: C 22.04; H 4.26; Si 26.07; Cl 31.70. M 551. $C_{10}H_{25}Si_5O_5Cl_5$. Calculated %: C 22.11; H 4.60; Si 25.80; Cl 32.71. M 542.5.

1,3,5-Triethyl-1-hydroxycyclotrisiloxane. A mixture of 11.1 g of 1,3,5-triethyl-1-chlorocyclotrisiloxane and 30 g of dry ether was cooled in liquid nitrogen to −50°. The mixture was poured into 30 g of water, found in a separatory funnel and previously cooled to 1°. The funnel with contents was shaken vigorously for 10 seconds; then the ether layer was separated, washed 4 times with cold water until neutral to Congo, and filtered. After removing the ether and moisture by vacuum-distillation at 2 mm and 50° we obtained 9 g (88%) of product.

d_{20}^{20} 1.0588, n_D^{20} 1.4288, MR_D 57.9; calc. 57.3.
Found %: Si 35.38; OH 7.04. M 240. $C_6H_{18}Si_3O_4$. Calculated %: Si 35.30; OH 7.14. M 238.

The product distills at 112-114° (2 mm); however, here it shows slight decomposition, giving poorer analysis results.

The given compound can also be obtained by hydrolysis with water, containing sufficient NaOH to neutralize the liberated HCl.

1,3,5-Triethyl-1,3-dihydroxycyclotrisiloxane. From 5.06 g of the triethyl-1,3-dichlorocyclotrisiloxane we obtained in similar manner 3.0 g (68%) of the dihydroxyl derivative.

d_{20}^{20} 1.1207, n_D^{20} 1.4345, MR_D 58.9; calc. 57.6.
Found %: Si 32.00; OH 13.72. M 248. $C_6H_{18}Si_3O_5$. Calculated %: Si 33.09; OH 13.40. M 254.

SUMMARY

The chlorination of some ethylcyclosiloxanes was studied, 7 new cyclic compounds were synthesized, and their properties were described.

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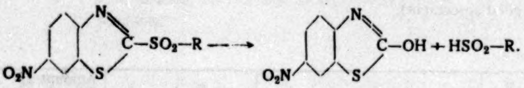
* T.p. = C. B. Translation pagination.

HYDROLYTIC CLEAVAGE OF SOME HETEROCYCLIC SULFONES

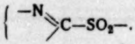
III. p-NITROPHENYL SULFIDES AND SULFONES OF BENZAZOLES AND 4-PHENYLPHTHALAZINE

N. P. Bednyagina and I. Ya. Postovsky

It was recently shown [1,2] that 6-nitro-2-benzothiazolyl aryl and alkyl sulfones suffer hydrolytic cleavage when heated in either acid or alkaline medium in accord with the scheme:



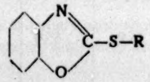
At the time we expressed the thought that this type of cleavage could also be typical of other heterocyclic sulfones, containing the sulfoazomethine grouping

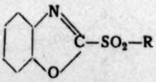


$\left(-\mathrm{N}{=}\mathrm{C}{-}\mathrm{SO_2}{-} \right)$.

Such a postulation had to be verified on various heterocyclic sulfones.

In this paper we describe the syntheses and compare the properties of the p-nitrophenyl sulfides and sulfones of some benzazoles (I, II, Ia-IIIa) and of 4-phenylphthalazine (IV-IVa), and also the results of the hydrolytic cleavage of the sulfones in alkaline medium.

(I)


(Ia)


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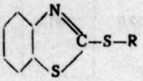
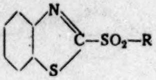
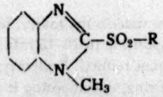


(IIa)


(IIIa)


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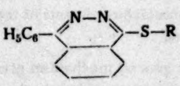
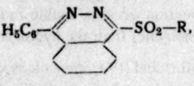
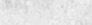


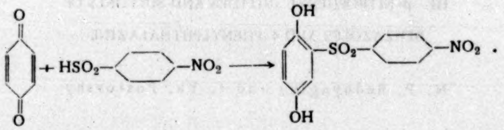
(IVa)


where R =


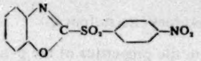
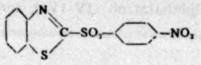
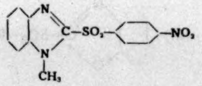
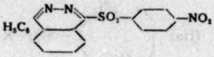
It was found that all of the obtained sulfides are stable, and do not show change when heated for several hours with either dilute alkalies or acids, whereas the sulfones under the same conditions suffer hydrolytic cleavage in accord with the above scheme.

Sine one "half" of the molecule is the same (p-nitrophenyl) in these compounds, it was also possible to simultaneously follow the influence of the heterocycle on the stability of the C–S bond by comparing the relative stability of these compounds toward hydrolysis.

The general hydrolysis product for all of the studied sulfones, namely p-nitrophenylsulfinic acid, was isolated as the adduct to benzoquinone [1] (2,5-dihydroxy-4'-nitrodiphenyl sulfone)



The sulfones were hydrolyzed in alkaline medium: a 0.500 g sample of the sulfone was heated for 30 minutes at 100° in 25 ml of 2N NaOH. The experimental results are given in the table (averages of three parallel experiments showing good agreement).

Substance No.	Sulfone	Amount of unchanged sulfone recovered (in %)	Cleaved (in %)	Amount of 2,5-dihydroxy-4'-nitrodiphenyl sulfone isolated (in % of the theoretical)
(Ia)		—	100	24
(IIa)		44.0	56.0	65
(IIIa)		45.0	55.0	72
(IVa)		19.0	81.0	75

As can be seen from the data in the table, the most easily cleaved is the benzoxazole sulfone (Ia). It already shows complete decomposition in 10-15 minutes of heating with 2N NaOH. However, the hydrolysis of this sulfone gives somewhat different results. Evidently, here the hydrolyzing agent attacks not only the C–S bond, but also the unstable oxazole ring, decomposing it with the formation of o-aminophenol, which was isolated in 80% yield. In this connection we were unable to isolate appreciable amounts of the p-nitrophenylsulfinic acid (as the adduct to benzoquinone) from the hydrolysis products.

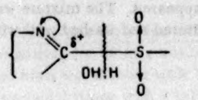
Sulfones (IIa), (IIIa) and (IVa) show cleavage by the general mechanism given above. The sulfone of benzothiazole (IIa) and of 1-methylbenzimidazole (IIIa) show approximately the same stability. The sulfone of the phenylphthalazine (IVa) is less stable. In the last case a second hydrolysis product, 4-phenylphthalazone, was isolated in 97% yield from the hydrolyzate.

As a result, there is basis to assume that the capacity for hydrolytic cleavage.is a general property of the sulfones that have a sulfoazomethine grouping with the azomethine portion in the cycle. In these compounds the C–S bond is weakened due to the simultaneous influence of two electronegative groups ($-N=C$ and $-SO_2$), the same as the C–C bond is weakened in chloral.

The instability of the bond between the benzothiazole ring and the sulfo group was observed by Efros and Davidenkov [3] for the case of 2-benzothiazolesulfonic acid. Here the sulfo group is replaced with unusual ease by nucleophilic substituents.

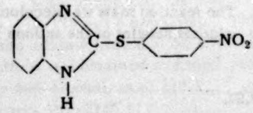
The above authors explain this instability of the $C-SO_2OH$ bond as being due to the concentration of a positive charge on the carbon atom connected to the sulfo group.

In the case of the above described sulfones the relative stability shown by each sulfone toward hydrolysis is probably also a function of the magnitude of the positive charge on the carbon atom attached to the sulfone radical.

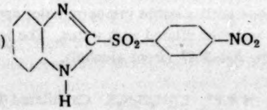


As can be seen from a comparison of the hydrolysis results obtained for sulfones (Ia–IVa), the character of the heterocycle shows substantial influence on the stability of the C–S bond. In addition, the structural characteristics of the heterocycle can also substantially change the hydrolysis course. Thus, the p-nitrophenyl benzimidazolyl sulfone (Va), showing a strongly acidic character, gives a crystalline sodium salt with alkali, which resinifies when heated in alkaline solution. In this case we were unable to isolate any individual hydrolysis products.

(V)

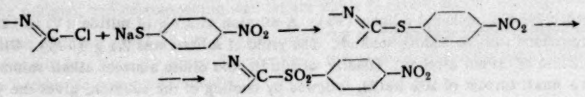


(Va)

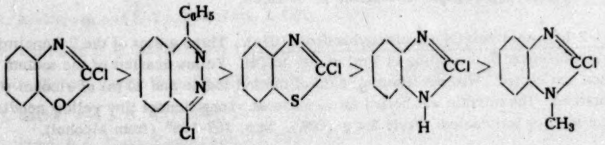


Of interest is the fact that in contrast to the sulfone, the corresponding sulfide (V), contrary to expectation, is insoluble in cold alkali, although the benzimidazole heterocycle itself, as is known, is readily soluble in it.* We were also unable to methylate the sulfide with methyl iodide, whereas the sulfone is easily methylated in alkaline medium and gives 1-methyl-benzimidazolyl p-nitrophenyl sulfone (IIIa). This peculiar difference between sulfide (V) and sulfone (Va) deserves further study.

The sulfones needed for our study were obtained by the oxidation of the corresponding sulfides, which in turn were obtained from the chloro-substituted heterocycles and sodium p-nitrothiophenolate.



Based on their relative reactivity the chloro derivatives can be arranged in the following order:



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*The sulfides go into solution when boiled with dilute sodium hydroxide, and on cooling the crystalline sulfides deposit in unchanged form.

In general the last chloride did not react even when boiled for 5 hours in alcohol with sodium p-nitrothiophenolate, and the corresponding sulfone (IIIa) was obtained only by the methylation of sulfone (Va). 1-Methyl-2-benzimidazolyl 4-nitrophenyl sulfide, corresponding to sulfone (IIIa), was not obtained; we were unable to obtain it either from sulfide (V), since this sulfide does not methylate, or from 1-methyl-2-chlorobenzimidazole, since the latter does not react with sodium p-nitrothiophenolate.

From a comparison of the hydrolysis data for the sulfones and the reactivity of the chlorides, it can be seen that in their reactivity the sulfones and the chlorides can be arranged in the same order.

When the sulfides are compared with the corresponding sulfones, attention is drawn to the fact that all of the sulfides are bright yellow in color, while their corresponding sulfones are colorless. Evidently, in the sulfides the sulfur atom with its unshared electron pairs functions as a conjugation link, and as a result, transfers the influence of the p-nitro group, while for the sulfones the $-SO_2$ group breaks the conjugation chain.

EXPERIMENTAL

2-Benzoxazolyl 4-nitrophenyl sulfide (I). To a solution of 5 g of 2-chlorobenzoxazole (b.p. 200° [4]) in 50 ml of anhydrous alcohol was added 6 g of sodium p-nitrothiophenolate. The mixture was stirred and heated at 50-60° for 30 minutes. The brown color of the p-nitrothiophenol quickly disappeared. The mixture was diluted with water and then made alkaline. The yellow sulfide precipitate was filtered and washed well with water. Yield 6.8 g (80%). Large yellow plates with m.p. 94-97° (from alcohol).

Found %: N 10.85. $C_{13}H_8O_3N_2S$. Calculated %: N 10.26.

2-Benzoxazolyl 4-nitrophenyl sulfone (Ia). A solution of 4 g of the benzoxazolyl p-nitrophenyl sulfide in 50 ml of glacial acetic acid was oxidized at room temperature with 7% $KMnO_4$ solution. An excess of $KMnO_4$ solution was added until a stable raspberry color appeared. The reaction mass was decolorized with sodium bisulfite solution and then diluted with water. The resulting colorless needles of the sulfone were filtered. Yield 3 g (70%). M.p. 204-205° (from alcohol).

Found %: N 9.67. $C_{13}H_8O_5N_2S$. Calculated %: N 9.21.

2-Benzothiazolyl 4-nitrophenyl sulfide (II) and sulfone (IIa). Both were obtained by the earlier described method [2,5].

2-Benzimidazolyl 4-nitrophenyl sulfide (V). A mixture of 6 g of 2-chlorobenzimidazole (m.p. 212° [6]) and 7.2 g of sodium p-nitrothiophenolate in 100 ml of alcohol was boiled for 2 hours. The sulfide was isolated in the same manner as in the preceding. Yield 7.7 g (75%). Large yellow needles with m.p. 182-183° (from alcohol). The sulfide does not dissolve in boiling aqueous alkali and remains unchanged when heated with CH_3I in alkaline medium.

Found %: N 15.84. $C_{13}H_9O_2N_3S$. Calculated %: N 15.48.

2-Benzimidazolyl 4-nitrophenyl sulfone (Va). A solution of 2.7 g of sulfide (V) in 130 ml of glacial acetic acid was oxidized with 7% $KMnO_4$ solution. The yield of sulfone was 2.1 g (70%). Glistening colorless plates with m.p. 222-223° (from alcohol). Readily soluble in cold dilute aqueous alkali solutions. Heating of the sulfone with a small amount of 20% NaOH, followed by cooling of the solution, gives the yellow crystalline sodium salt, readily soluble in water.

Found %: N 13.05. $C_{13}H_9O_4N_3S$. Calculated %: N 13.08.

1-Methyl-2-benzimidazolyl 4-nitrophenyl sulfone (IIIa). Three grams of the 2-benzimidazolyl 4-nitrophenyl sulfone was dissolved with heating in 5 ml of 20% NaOH. Yellow leaflets of the sodium salt deposited when the solution was cooled. Without filtering, 5 ml of methyl iodide and 20 ml of alcohol was added until solution was obtained. The mixture was boiled for 30 minutes. Long slender tiny yellow needles of (IIIa) deposited when the solution was cooled. Yield 2.4 g (80%). M.p. 167-168° (from alcohol).

Found %: N 13.48. $C_{14}H_{11}O_4N_3S$. Calculated %: N 13.24.

4-Phenyl-1-phthalazinyl 4-nitrophenyl sulfide (IV). To a suspension of 3.6 g of 4-phenyl-1-chlorophthalazine (m.p. 160-161° [7]) in 50 ml of alcohol was added 2.6 g of sodium p-nitrothiophenolate. The reaction mass was boiled for 30 minutes and then diluted with 100 ml of water. Yield of sulfide 5.4 g (97%). Coarse yellow needles with m.p. 158-160° (from a mixture of alcohol and benzene).

Found %: N 11.86. $C_{20}H_{13}O_2N_3S$. Calculated %: N 11.69.

4-Phenyl-1-phthalazinyl 4-nitrophenyl sulfone (IVa). A solution of 3.6 g of sulfide (IV) in 100 ml of glacial acetic acid was oxidized with 7% $KMnO_4$ solution. The yield of (IVa) was 2 g (50%). Colorless crystals with m.p. 147-150° (from alcohol).

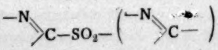
Found %: N 10.72. $C_{20}H_{13}O_4N_3S$. Calculated %: N 10.73.

Hydrolytic cleavage of sulfones. The sulfones (0.500 g samples) were heated with 25 ml of 2N NaOH under stirring for 30 minutes in a small flask under reflux on a water-salt bath at 100° (in the bath). The reaction mass was diluted with 10 ml of water and then cooled. The deposit of unchanged sulfone was filtered and washed 3 times with 3 ml portions of water. The filtrate was acidified with concentrated HCl until slightly acid to litmus.

Hydrolysis of sulfone (IVa) gave the phenylphthalazone as a precipitate, m.p. 232-233°; its melting point was not depressed when mixed with the product of authentic structure. Hydrolysis of sulfone (Ia) gave o-aminophenol (m.p. 170-173°) as a precipitate. The acid filtrate was treated with 0.1 g of finely powdered benzoquinone and the mixture heated at 50-60° with stirring. Here the quinone dissolved and the 2,5-dihydroxy-4'-nitrodiphenyl sulfone was obtained as a light yellow microcrystalline precipitate. M.p. 205-210°. After recrystallization from 50% alcohol, m.p. 210-211°, and its melting point was not depressed when mixed with the synthetic product (m.p. 210-211° [1]).

SUMMARY

1. We synthesized the p-nitrophenyl sulfides and sulfones of 2-benzoxazole (I, Ia), 2-benzothiazole (II, IIa), 2-benzimidazole (V, Va) and 4-phenyl-1-phthalazine (IV, IVa), and the p-nitrophenyl sulfone of 1-methyl-2-benzimidazole (IIIa).

2. Sulfones (Ia)-(IVa) when heated in alkaline medium show hydrolytic cleavage with the formation of p-nitrophenylsulfinic acid. Evidently, the capacity for hydrolytic cleavage at the C-S bond is a general property of the sulfones containing the sulfoazomethine grouping  $\left(-N{=}C\langle\right)-SO_2-\left(-N{=}C\langle-\right)$ in the cycle In contrast to the sulfones, the corresponding sulfides are stable to hydrolysis.

3. All of the obtained sulfides have a yellow color, while the sulfones are colorless. The theory is expressed that in the sulfides the -S- group functions as a link in the conjugation chain, whereas in the sulfones the $-SO_2-$ group breaks the conjugation chain.

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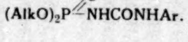
*T.p. = C. B. Translation pagination.

CHLORIDES AND ESTERS OF ARYLCARBAMIDOPHOSPHORIC ACIDS

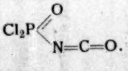
A. V. Kirsanov and E. S. Levchenko

The purpose of the present investigation was to obtain and study the properties of the arylcarbamidophosphoric acid esters of general formula:

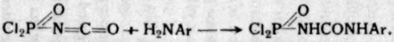


$$(AlkO)_2P(=O)NHCONHAr.$$

The starting product for the synthesis of this group of compounds was the recently obtained [1] chloride of isocyanatophosphoric



The chloride of isocyanatophosphoric acid, the same as organic isocyanates, is capable of reaction with aromatic amines. With equimolar proportions of the reactants the amine adds to the isocyanate group with the formation of the chlorides of arylcarbamidophosphoric acids:

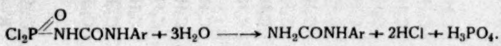


$$Cl_2P(=O)N{=}C{=}O + H_2NAr \longrightarrow Cl_2P(=O)NHCONHAr.$$

The addition goes very smoothly, and the reaction products deposit from ether solution in measure with amine addition. The aromatic amines with negative substituents show somewhat slower reaction. Thus, when the chloride of isocyanatophosphoric acid is reacted with o- and m-nitroaniline, p-bromo- and p-chloroaniline, 2,4,6-trichloroaniline and 2,4-dinitrotoluidine, the reaction products begin to deposit within 1-2 minutes after mixing the ether solutions of the starting substances. The secondary amines (diphenylamine) enter into this reaction with somewhat greater difficulty.

The obtained compounds, their yields, melting points and analysis data are given in Table 1.

The chlorides of the arylcarbamidophosphoric acids are crystalline compounds, difficultly soluble in benzene, ether, carbon tetrachloride and chloroform. They slowly decompose in the air. They react slowly with water at room temperature, while under heating the hydrolysis proceeds rapidly. The water adds mainly at the P–N bond, since the main hydrolysis products are the N-arylureas:



$$Cl_2P(=O)NHCONHAr + 3H_2O \longrightarrow NH_2CONHAr + 2HCl + H_3PO_4.$$

Exceptions are the chlorides of N,N-diphenylcarbamidophosphoric acid and N,N-phenylethylcarbamidophosphoric acid. When they are hydrolyzed the main products are respectively diphenylamine and ethylaniline, and only small amounts of diphenyl- and ethylphenylureas are obtained. All of the chlorides of the arylcarbamidophosphoric acids titrate as 4 equivalents when titrated with sodium hydroxide solution in the presence of

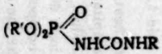
TABLE 1

Expt. Nos.	R	Decomposition temperature	Yield (in %)	External appearance	Empirical formula	Chlorine content (in %)		Equivalent determination
						found	calc.	
				Chlorides of Arylcarbamidophosphoric Acids — $Cl_2PONHCONHR$				
1	C_6H_5	124—125°	99.0	Colorless prisms	$C_7H_7O_2N_2Cl_2P$	28.03, 27.69	28.06	3.99, 4.02
2	$C_6H_4CH_3$-p	120	98.0	Thin plates	$C_8H_9O_2N_2Cl_2P$	26.14, 26.09	26.56	3.82, 3.98
3	$C_6H_4CH_3$-*o*	117—118	61.8	Coarse colorless crystals	$C_8H_9O_2N_2Cl_2P$	26.47, 26.40	26.56	3.99, 4.01
4	$C_6H_4C_2H_5$-p	127—128	93.0	Transparent colorless crystals	$C_9H_{11}O_2N_2Cl_2P$	24.80, 24.66	25.23	4.01, 4.02
5	$C_6H_4C_3H_7$-iso.-p	128—130	85.6	Rhombohedral prisms	$C_{10}H_{13}O_2N_2Cl_2P$	24.23, 23.72	24.04	3.99, 4.00
6	$C_6H_4OCH_3$-p	118—120	81.0	Colorless microcrystalline powder	$C_8H_9O_3N_2Cl_2P$	24.82, 24.67	25.06	4.05, 4.00
7	$C_6H_4OC_2H_5$-p	122—124	71.0	Colorless microcrystalline powder	$C_9H_{11}O_3N_2Cl_2P$	23.69, 23.40	23.87	3.97, 3.99
8	$C_6H_4NO_2$-*o*	146—147	74.2	Yellow scaly crystals	$C_7H_6O_4N_3Cl_2P$	23.98, 23.85	23.80	—
9	$C_6H_4NO_2$-m	161—162	86.5	Colorless plates	$C_7H_6O_4N_3Cl_2P$	23.97, 24.18	23.80	—
10	$C_6H_4NO_2$-p	160	73.8	Lemon yellow microcrystalline powder	$C_7H_6O_4N_3Cl_2P$	23.83, 23.87	23.80	—
11	$C_6H_3CH_3(4)NO_2(2)$	155—157	85.0	Long thin light yellow plates	$C_8H_8O_4N_3Cl_2P$	22.55, 22.72	22.73	—
12	C_6H_4Cl-p	147—148	83.7	Fine needles	$C_7H_6O_2N_2Cl_3P$•	24.96, 24.89	24.66	3.93, 4.07
13	C_6H_4Br-p	149—150	91.3	Colorless plates	$C_7H_6O_2N_2Cl_2BrP$	21.07, 20.73	20.88	3.98, 3.99
14	$C_6H_2Cl_3(2,4,6)$	155—158	89.9	Elongated plates	$C_7H_4O_2N_2Cl_5P$•	19.90, 19.94	19.90	3.98 —
15	$C_{10}H_7$-α	123—125	61.8	Colorless microcrystalline powder	$C_{10}H_9O_2N_2Cl_2P$	23.19, 23.21	23.40	3.89, 3.92
16	$C_{10}H_7$-β	137—138	87.0	Colorless prisms	$C_{10}H_9O_2N_2Cl_2P$	23.30, 23.04	23.40	3.90, 3.89
				Chlorides of Arylcarbamidophosphoric Acids — $Cl_2PONHCONR'R''$				
17	$R'=C_2H_5, R''=C_6H_5$	137	92.3	Transparent needles	$C_9H_{11}O_2N_2Cl_2P$	21.07, 20.73	20.88	3.94, 3.96
18	$R'=R''=C_6H_5$	113—114	68.5	Coarse colorless prisms	$C_{13}H_{11}O_2N_2Cl_2P$	25.40, 25.35	25.23	3.94 —

•Hydrolyzable chlorine was determined.

TABLE 2

Esters of Arylcarbamidophosphoric Acids



$(R'O)_2P(=O)NHCONHR$

Expt. Nos.	R	R′	Melting point	Yield (in %)	External appearance	Empirical formula	Nitrogen determination (in %)	
							found	calc.
1	C_6H_5	CH_3	135—136°	45.2	Colorless needles from water	$C_{19}H_{13}O_4N_2P$	11.50, 11.54	11.47
2	C_6H_5	C_2H_5	125—127	30.0	Needles from methyl alcohol	$C_{11}H_{17}O_4N_2P$	10.35, 10.40	10.29
3	C_6H_5	C_3H_7-iso	138—140	9.6	Needles from methyl alcohol	$C_{13}H_{21}O_4N_2P$	9.32, 9.26	9.33
4	$C_6H_4CH_3$-p	CH_3	135—138	24.2	Plates from methyl alcohol	$C_{10}H_{15}O_4N_2P$	10.81, 10.62	10.86
5	$C_6H_4CH_3$-o	CH_3	116—117	49.0	Colorless plates from water	$C_{10}H_{15}O_4N_2P$	10.96, 11.14	10.86
6	$C_6H_4C_2H_5$-p	CH_3	126—128	71.0	Plates from methanol	$C_{11}H_{17}O_4N_2P$	10.23, 10.33	10.30
7	$C_6H_4C_3H_7$-iso-p	CH_3	145—148	64.8	Needles from aqueous ethanol (1: 1)	$C_{12}H_{19}N_2O_4P$	9.77, 9.69	9.79
8	$C_6H_4OCH_3$-p	CH_3	148—149	58.6	Prisms from benzene	$C_{10}H_5O_5N_2P$	10.12, 10.25	10.21
9	$C_6H_4OC_2H_5$-p	CH_3	147—149	58.0	Needles from benzene	$C_{11}H_{17}O_5N_2P$	9.45, 9.33	9.72
10	$C_6H_4NO_2$-o	CH_3	165—166	83.0	Light yellow plates from methanol	$C_9H_{12}O_6N_3P$	14.57, 14.80	14.53
11	$C_6H_4NO_2$-m	$C\ _3$	165—167	51.0	Colorless needles from methanol	$C_9H_{12}O_6N_3P$	14.46, 14.52	14.53
12	$C_6H_4NO_2$-p	CH_3	176—177	50.0	Light yellow crystals from methanol	$C_9H_{12}O_6N_3P$	14.66, 14.49	14.53
13	$C_6H_3CH_3(4)NO_2(2)$	CH_3	180—181	70.0	Yellow needles from methanol	$C_{10}H_{14}O_6N_3P$	13.87, 13.91	13.86
14	C_6H_4Cl-p	CH_3	139—140	58.3	Colorless needles from methanol	$C_9H_{12}O_4N_2ClP$	9.87, 9.68	10.05
15	C_6H_4Br-p	CH_3	144—146	88.0	Plates from benzene	$C_9H_{12}O_4N_2BrP$	8.81, 8.95	8.66
16	$C_6H_2Cl_3(2,4,6)$	CH_3	159—161	44.0	Colorless crystals	$C_9H_{10}O_4N_2Cl_3P$	8.25, 8.39	8.05
17	$C_{10}H_7$-α	CH_3	155—156(decomp)	81.7	Plates from methanol	$C_{13}H_{15}O_4N_2P$	9.39, 9.60	9.52
18	$C_{10}H_7$-β	CH_3	164—165	62.0	Colorless crystals from benzene	$C_{13}H_{15}O_4N_2P$	9.28, 9.24	9.52

either phenolphthalein or thymolphthalein. With alcoholates the chlorides of the arylcarbamidophosphoric acids gives the corresponding esters:

$$Cl_2PONHCONHAr + 2R'ONa \longrightarrow (R'O)_2PONHCONHAr + 2NaCl.$$

If the starting substances are taken in a 1:3 molar ratio, then as a result of reaction,sodium salts that are readily soluble in water are obtained. A similar phenomenon was observed in obtaining the esters of arylsulfonamidophosphoric acids $ArSO_2NHPO(OR)_2$ [2].

The sodium derivatives of the arylcarbamidophosphoric acid esters, obtained during reaction, are usually quite soluble in benzene, which was used as the solvent. However, in preparing the dimethyl esters of the p-bromophenyl- and m-nitrophenylcarbamidophosphoric acids, the sodium derivatives deposited in the precipitate under the reaction conditions, the precipitate going into solution when water was added. The obtained arylcarbamidophosphoric acid esters, their melting points, yields, and analysis data are presented in Table 2.

The arylcarbamidophosphoric acid esters are crystalline compounds. Most of them are readily soluble in methyl and ethyl alcohols, and more difficultly soluble in benzene and ether. Esters 1, 4, 6 and 10 (Table 2) go into solution when heated in water. Like the arylsulfonamidophosphoric acid esters [2], they show acidic properties, being readily soluble in aqueous alkali. The arylcarbamidophosphoric acid esters, containing a nitro group in the benzene ring (10, 11, 12, 13), dissolve in alkali with an orange color.

Under prolonged boiling with water the arylcarbamidophosphoric acid esters decompose with the evolution of carbon dioxide. An aromatic amine is one of the hydrolysis products (see Experimental section).

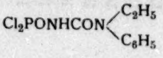
EXPERIMENTAL

Chlorides of Arylcarbamidophosphoric acids. To an ether solution of the chloride of isocyanatophosphoric acid (0.05 mole in 50 ml of ether) was slowly added with cooling an ether solution of an equimolar amount of the aromatic amine in 50 ml of ether. After 20-30 minutes the obtained precipitate was filtered, washed with ether, and dried in a vacuum-desiccator in the presence of phosphorus pentoxide. The freshly prepared compounds were analyzed.

The obtained products, their melting points, yields, and analysis data are presented in Table 1.

Hydrolysis of arylcarbamidophosphoric acid chlorides. The hydrolysis was run under slight heating of the starting product with water. The reaction product, in most cases depositing as a crystalline precipitate, on cooling the reaction mixture was filtered, washed with a small amount of water, and dried. The product, obtained in the hydrolysis of the chloride of N,N-diphenylcarbamidophosphoric acid, was steam-distilled; here diphenylamine steam-distilled, while the N,N-diphenylurea remained in the distillation flask. The obtained compounds were identified either by their mixed melting points with authentic compounds or by comparison with the data given in the literature for the melting points. The hydrolysis results obtained for some of the arylcarbamidophosphoric acid chlorides are presented in Table 3.

TABLE 3

Expt. nos.	Formula	Hydrolysis product	Yield (in%)	Melting point	Literature references
1	$Cl_2PONHCONHC_6H_5$	$H_2NCONHC_6H_5$	46	146—147°	—
2	$Cl_2PONHCONHC_6H_4OCH_3$-p	$H_2NCONHC_6H_4OCH_3$-p	57	165—166	[3]
3	$Cl_2PONHCONHC_6H_4NO_2$-*o*	$H_2NCONHC_6H_4NO_2$-*o*	89	132—134	[4]
4	$Cl_2PONHCONHC_6H_4NO_2$-p	$H_2NCONHC_6H_4NO_2$-p	95	237—238	[5]
5	$Cl_2PONHCON(C_6H_5)_2$	$(C_6H_5)_2NH$	50	51—52	—
		$NH_2CON(C_6H_5)_2$	7.5	182—184	[6]
6	 $Cl_2PONHCON\begin{smallmatrix} C_2H_5 \\ C_6H_5 \end{smallmatrix}$	$C_6H_5NHC_2H_5$	55	132—133 (picrate)	—

Esters of arylcarbamidophosphoric acids. To a suspension of the arylcarbamidophosphoric acid chloride in benzene (usually 0.2-0.5 mole of the chloride in 30-60 ml of benzene was taken), was slowly added, with cooling, a solution of sodium alcoholate in the corresponding alcohol (the chloride and metallic sodium were taken for reaction in a mole ratio of 1:3). Two methods were used to isolate the reaction products: 1) the reaction mixture was treated with water, the benzene layer was separated, and acidification of the water extract usually gave the carbamidophosphoric acid esters as oils, which then crystallized. 2) The benzene and excess alcohol were removed by distillation on the water bath, the residue was dissolved in water, and the reaction product was precipitated by acidification of the water solution. Esters 4, 10, 11 and 12 (Table 2) were isolated in this manner.

SUMMARY

1. The reaction of the chloride of isocyanatophosphoric acid with aromatic amines was studied. A number of arylcarbamidophosphoric acid chlorides were prepared and described.

2. The reaction of the chlorides of arylcarbamidophosphoric acids with the alcoholates of aliphatic alcohols was studied. A number of arylcarbamidophosphoric acid esters were prepared and described.

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*T.p. = C. B. Translation pagination.

APPLICATION OF THE HOFFMAN REACTION TO HIGH-MOLECULAR COMPOUNDS CONTAINING AMIDE GROUPS

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In the present investigation we studied the possibility of obtaining high-molecular compounds containing primary amino groups in the side chain, by the method of hypobromite decomposition of amides, known as the Hofmann reaction.

With the exception of one exploratory experiment [1], studies devoted to the application of the Hofmann reaction for obtaining primary amino groups in the side chains of high-molecular compounds are absent in the literature. In the indicated study an attempt was made to obtain polyvinylamine from polyacrylamide by the method of hypobromite decomposition in water solution.

The main product contained a small amount of amino groups, a considerably larger amount of carboxyl groups, probably alkylacylurea groups, and also some unreacted amide groups. The obtained substance was soluble in water and dilute acids.

After our work had been already completed, a paper was published [2], in which both the hypobromite and hypochlorite decomposition of polymethacrylamide in aqueous solution had been studied. The obtained products contained a small amount of amino groups, a considerably larger amount of carboxyl groups, supposedly alkylacylurea groups, and some unreacted amide groups. The amount of structural links with primary amino groups did not exceed 5.5%.

Consequently, the indicated studies cannot be considered as being fully successful. The authors did not make sufficient use of the conditions of similar transformations, known for low-molecular compounds. From the literature [3] it is known that in alcohol medium it is possible to avoid secondary reactions, including the reactions of alkylacylurea formation and the premature hydrolysis of the amide groups.

Taking the above into account, the hypobromite decomposition reaction was run in alcohol medium using an excess of bromine and alkali, which in some cases improve the yield [4].

To defend ourselves it is necessary to mention that our problem was to obtain a high-molecular compound, at the same time also containing carboxyl groups, for which reason in running the reaction we limited ourselves to obtaining a comparatively small content of primary amino groups, in sufficient amount so that we could determine their influence on some properties of the obtained compound.

We selected divinylacrylonitrile rubber as our starting material. For converting the nitrile groups of the divinylacrylonitrile rubber we used the method of Badanina and one of the authors [5]. However, the first experiments on the hypobromite decomposition of the amide groups formed in the partial saponification of the nitrile groups did not give the desired result. Later we developed methods for obtaining amide groups from nitrile groups by treating the nitriles with either alkaline peroxide or water under pressure and at a temperature of 180°. The particular methods and results are described in the literature [6].

In the main, for subsequent studies of the applicability of the Hofmann reaction, we took partially saponified divinylacrylonitrile rubber that had been subjected to treatment with water at 180° under pressure, and having a total nitrogen content of 7.47% (the total nitrogen content of the original untreated rubber was 10.1%).

EXPERIMENTAL

The hypobromite decomposition was run under various conditions so as to assure obtaining a high yield of amino nitrogen. The time of treatment with hypobromite was varied, the duration of subsequent treatment with alkali, the temperature, etc. Below we describe one of the methods used, with a variable duration of the treatment with hypobromite and alkali.

To a solution of 225 g of KOH in 1700 ml of ethyl alcohol with cooling and constant stirring was slowly added 43 ml of bromine, and then 300 g of the starting high-molecular substance, containing amide groups, was added. The flask was stoppered and kept in an ice bath for 24 hours, after which the mixture was heated at the boil for 4-10 hours. The obtained product was washed with water, dried, and then treated with alkali.

The purpose of the subsequent alkaline treatment was to decompose the urethane groupings, formed in the treatment with alcoholic hypobromite solution, and convert them into primary amino groups. For this the obtained substance was placed in a flask with 40% NaOH solution and the mixture was heated at the boil for 4 hours. Here 100 g of substance required 400 ml of the NaOH solution.

The obtained products were washed for 2 days with water and then their degree of swelling in 0.1 N NaOH and HCl solutions was determined. The relationship between the swelling ability and the treatment regime can be seen from the table.

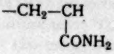
Sample No.	Duration of treatment (in hrs)		Percent swelling in 0.1 N	
	hypobromite	alkali	NaOH	HCl
1	4	4	222	151
2	6	4	140	128
3	4	2	122	122
4	4	4	380	184
5	4	12	1260	191
6	10	4	840	169
7	4	4	461	187

From the data in the table it can be seen that an increase in the time of hypobromite treatment does not appreciably increase the content of basic groups, and gives a difference increase in the degree of swelling in acid and alkali, in the main due to hydrolysis of the nitrile groups to carboxyl groups. An increase in the duration of treatment with alkali also leads to an increase in the amount of carboxyl groups.

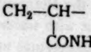
For the purpose of creating milder conditions for the cleavage of the urethane groups an attempt was made to treat the product with less concentrated NaOH solutions. Treatment with 20% alkali for 6 hours at the boil gave a substance with a swelling value of 160% in 0.1 N NaOH, and one of 130% in 0.1 N HCl, i.e. with extremely close swelling values.

Taking into consideration the fact that in the hypobromite decomposition process, and especially in the subsequent treatment with alkali, ammonia is liberated, an attempt was made to run the hypobromite and alkali treatments in the presence of ammonia. When this was done we obtained a product with a swelling value of 115% in 0.1 N NaOH, and one of 100% in 0.1 N HCl. The retarding role played by ammonia is quite evident from this, first of all in the saponification of the nitrile groups. Determination of amino nitrogen by the modified Van Slyke method [7] gave the following results: Sample 4, 0.82%; Sample 7, 0.65% (see table). If it is considered that the total nitrogen content of the starting, partially saponified divinylacrylonitrile rubber was 7.47%, then it follows that we succeeded in converting 9-10% of the links, containing nitrile groups, through the amide stage into links containing primary amino groups.

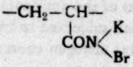
The following products (I-VI) [8] can be obtained when the hypobromite decomposition reaction in alcohol medium is applied to the investigated product:


$-CH_2-CH(CONH_2)$

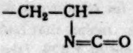
(I)


$CH_2-CH(CONHBr)-$

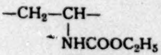
(II)


$-CH_2-CH(CON(K)(Br))-$

(III)


$-CH_2-CH(N{=}C{=}O)-$

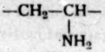
(IV)


$-CH_2-CH(NHCOOC_2H_5)-$

(V)

• The differences in the degree of swelling shown by samples 1, 4 and 7 can be explained by some differences in the preliminary treatment conditions (prior to the hypobromite).

Since the hypobromite decomposition reaction in alcohol medium is terminated by the formation of urethane groups, then either alkaline or acid treatment is needed for their decomposition and conversion into primary amino groups (VI).



$$-CH_2-\underset{\displaystyle NH_2}{\underset{|}{CH}}-$$

(VI)

However, the indicated main reaction is accompanied by a number of secondary reactions, in some cases considerably lowering the yield. The formation of symmetrically substituted cyclic ureas and the formation of bonds between chain molecules, due to linkage of secondary amino groups with the α-carbon hydrogen atoms of adjacent chains, can be cited as belonging to such reactions. It is evident that the main reason for the low amino nitrogen content must be considered to be the low yield of amide groups in the saponification of the nitriles.

On the basis of the data for the total nitrogen content of the starting and final products in the reaction scheme, and the data on the amount of amino nitrogen, an approximate estimate can be made of the proportions of the main structural elements that enter into the composition of one of the obtained products (see table, Sample 7).

Calculation gives the following proportions: $(C_4H_6)_{16.2}$, $(C_2H_3CN)_{4.5}$, $(C_2H_3COOH)_{4.6}$, $(C_2H_3NH_2)_1$.

This product was studied for the purpose of investigating some of its properties, determined by the presence of carboxyl and amine groups. Since the last treatment was with alkali, the obtained product was first of all washed free of alkali with a running stream of water until bleached (several hours), and then with a periodic change of the water. The alkali is removed with comparative rapidity during the first 4-5 days, and then it is markedly retarded. Only after 28 days was a neutral reaction to phenolphthalein obtained, although even at this stage the obtained substance had an ash-content of 5.9% and an alkalinity of 0.91%.

Interesting data were obtained when the acid and alkali capacities were determined. For this 1 g of finely pulverized, reduced to constant weight, product was placed in a flask with ground-glass stopper, where 35 ml of 0.1 N NaOH (or hydrochloric acid) was then added. After 72-hour standing at room temperature the unabsorbed alkali (or acid) was titrated.

The determination results (making allowance for the ash-content of the product) were: alkali capacity, 0.96 mg-equiv./g; acid capacity, 0.43 mg-equiv/g.

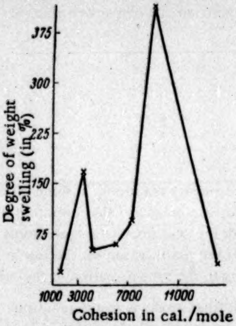
When the amounts of basic and acidic groups were compared, calculated on the basis of the alkali and acid capacities, and also on the determination data of total and amino nitrogen, it was found that the amount of groups reacting under the given conditions is considerably less than the amount calculated from the total and amino nitrogen: only one half of the amino groups react, and only one third of the carboxyl groups.

A very interesting agreement in the results of determining the alkali capacity and alkalinity of the product should be mentioned. If the alkali capacity (taking into account the alkalinity of the product) is calculated on the basis of the alkalinity, then it proves to be equal to 6.07%, instead of 5.9%.

Determination of the bromine number of the obtained substance revealed that in it the double bonds, existing in the original divinyl acrylonitrile rubber, remained unchanged.

A study of the behavior of the obtained product toward a large number of solvents revealed that even after 4 days it did not dissolve in any of them. Only partial solution was observed when it was kept for a long time (more than a month) in a mixture of phenol and water. This indicates the spatial ("sewn") structure of the given substance.

If the data on the degree of swelling in different solvents are compared with the molar cohesion values of the active groups [9], then the curve shown in the figure can be obtained; from this it can be seen that the swelling of the studied product is characterized by the presence of two maxima – for molar cohesions of 3530 cal/g-mole and 8970 cal/g-mole, which correspond to compounds that have both primary amino and carboxyl groups in their composition.



Relationship between the degree of swelling and the molar cohesion.

When a certain amount of alkali is introduced, the studied product is easily dispersed in water when worked on rolls or in a colloid mill. A study of the dispersions, obtained by the two methods, revealed that their stability with time is very great, especially the dispersion obtained in the colloid mill. The addition of acid gave a precipitate, which again was easily dispersed under the influence of alkali.

As a result, the structure of the studied product, the peculiarities of obtaining the aqueous dispersion (absence of stabilizer, previous swelling, etc.), and the unique properties of the dispersion (high stability) placed it in a special position when compared with the usual dispersions of hydrophobic substances in water. It constitutes somewhat of an average between a concentrated solution of a high-molecular compound and suspensions. It is evident that the formation of a true solution disturbs the three-dimensional structure of the studied product.

Because double bonds are present, the studied product is capable of reacting with sulfur to give an effect that is similar to the vulcanization of rubber: the stretch modulus is increased, the relative elongation is decreased, and the degree of swelling in solvents is reduced. Extremely interesting is the fact that a tanning effect can be achieved by treating this product with formaldehyde and chromium salts. Analysis of the samples treated with formalin gave a bound formaldehyde content of 0.24-0.33%. At the same time the swelling of the product in solvents was lowered with a marked reduction in the swelling maximum; also the degree of swelling in mineral acids and in alkalies was reduced. When cationic chrome liquor with a Cr_2O_3 content of 26.9% and a basicity of 34% was used for tanning, the studied substance showed a considerable decrease in the degree of swelling in solvents, acids and alkalies. The amount of bound Cr_2O_3 was 2.25%. The results, obtained with the two tanning methods, again needlessly demonstrate the presence of active amino and carboxyl groups.

SUMMARY

1. It was shown that in the alkaline hydrolysis of nitrile groups in high-molecular compounds the process is not retarded at the amide stage.

2. The use of the Hofmann reaction gave a number of products, containing a variable ratio of amino and carboxyl groups.

3. It was shown that the most effective way of running the Hofmann reaction to obtain high-molecular polyamines is to use alcoholic hypobromite solutions.

4. It was shown that the carboxyl and amino groups, introduced into the obtained product, differ sharply in activity.

5. Aqueous dispersions were obtained, which occupy an intermediate position between the solutions of high-molecular substances and aqueous dispersions of hydrophobic substances.

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HYDROGEN BOND AND PHYSICAL PROPERTIES OF NITROANILINES

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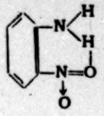
The physical properties of the melts of nitroanilines (Table 1) and of their solutions in benzene and ethanol (Table 2) are evidence that in some respects they are similar to the nitrophenols. The same as for the latter, o-nitroaniline shows sharply reduced values of the indicated properties when compared with p-nitroaniline; here the difference in the values of the indicated properties (at 172°) between o- and p-nitroanilines is numerically almost the same as the difference between the o- and p-nitrophenols (at 184°) [1]. Since a similar type of relationship between the values of the isomer properties is absent for the toluidenes, it is possible that the indicated behavior of the nitroanilines is associated with the fact that the ortho isomer, the same as is true for o-nitrophenol, contains an intramolecular hydrogen bond (I).



(I)

Its other properties also testify to the presence of such a bond for o-nitroaniline: a sharp reduction in its melting point, nearly the same as for o-nitrophenol [2], a relative vapor pressure (at 100°), ultraviolet absorption in a considerably longer wavelength region than the isomer [3], a reduced area of molar absorption in the N-H frequency region [4], etc.

TABLE 1

Physical Properties of Melts of Substituted Anilines*

Compound		$d_4^{t°}$		γ		$\eta \cdot 10^5$	
		131°	172°	131°	172°	131°	172°
$C_6H_5NH_2$		0.923	0.872	31.3	25.5	569	403
$C_6H_4(NH_2)CH_3$	o-	—	0.874	—	23.3	—	418
	m-	—	0.872	—	22.4	—	384
	p-	—	0.857	—	22.5	—	397
$C_6H_4(NH_2)NO_2$	o-	1.204	1.161	40.4	36.6	1437	919
	m-	1.208	1.171	41.9	38.5	1459	936
	p-	—	1.230	—	45.0	—	1436
$C_6H_5N(CH_3)_2$		0.861	0.827	24.8	20.5	416	318
$C_6H_4(NO_2)N(CH_3)_2$	o-	1.073	1.039	31.2	27.7	954	673
	m-	1.078	1.047	32.0	27.9	962	691
	p-	—	1.101	—	34.7	—	1015

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*d is the density, γ is the surface tension, η is the internal friction coefficient, and t° is the temperature.

That the nitroanilines and nitrophenols are similar also appears in the fact that the m- and p-nitroanilines, similar to the m- and p-nitrophenols, behave as intermolecularly associated compounds. Actually, in the isoperiodic series of compounds the m- and p- nitroanilines, similar to phenols and aromatic alcohols, show sharp deviation from the general rules valid for all normal liquids with respect to the changes in the values of γ, η and

TABLE 2

Physical Properties of Substituted Anilines in Benzene and Ethanol Solutions at 50° ± 0.1 (Sample Weight 0.9984-0.9990 g in ~ 25 ml of Solution)

Compound		d in		$\eta \cdot 10^6$ in	
		benzene	ethanol	benzene	ethanol
$C_6H_5NH_2$		0.8532	0.7893	463	738
$C_6H_4(NH_2)CH_3$	o-	0.8523	0.7938	459	729
	m-	0.8519	0.7937	456	727
	p-	0.8520	0.7940	452	725
$C_6H_4(NH_2)NO_2$	o-	0.8542*	0.8015	—	739
	m-	0.8543	0.8013	—	740
	p-	0.8549	0.8027	—	753
$C_6H_5N(CH_3)_2$		0.8505	0.7855	431	719
$C_6H_5(NO_2)N(CH_3)_2$	o-	0.8522	0.7983	—	717
	m-	0.8526	0.7986	—	—

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*Sample weight 0.5000 g.

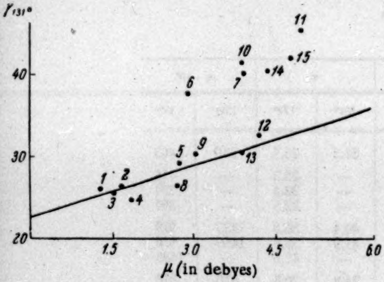


Fig. 1. Relationship between surface tension and dipole moment at 131°.

1 — $C_6H_4(OCH_3)_2$-o, 2 — $C_6H_4(OCH_3)_2$-p, 3 — $C_6H_5OCOCH_3$, 4 — $C_6H_5COOCH_3$, 5 — $C_6H_4(COCH_3)OH$-o, 6 — $C_6H_4(COCH_3)OH$-m 7 — $C_6H_4(COCH_3)OH$-p, 8 — $C_6H_5COC_6H_5$, 9 — $C_6H_4(NO_2)OH$-o, 10 — $C_6H_4(NO_2)OH$-m 11 — $C_6H_4(NO_2)OH$-p 12 — $C_6H_4(CHO)OCH_3$-o, 13 — $C_6H_4(CHO)OCH_3$-p, 14 — $C_6H_4(NO_2)NH_2$-o, 15 — $C_6H_4(NO_2)NH_2$-m

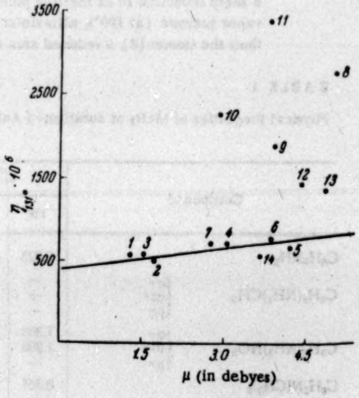


Fig. 2. Relationship between viscosity and dipole moment.

1 — $C_6H_4(OCH_3)_2$-o, 2 — $C_6H_4(OCH_3)_2$-p 3 — $C_6H_5OCOCH_3$, 4 — $C_6H_4(NO_2)OH$-o, 5 — $C_6H_4(CHO)OCH_3$-o, 6 — $C_6H_4(CHO)OCH_3$-p 7 — $C_6H_4(COCH_3)OH$-o, 8 — $C_6H_4(NO_2)OH$-p 9 — $C_6H_4(NO_2)OH$-m 10 — $C_6H_4(COCH_3)OH$-m 11 — $C_6H_4(COCH_3)OH$-p 12 — $C_6H_4(NO_2)NH_2$-o, 13 — $C_6H_4(NO_2)NH_2$-m 14 — $C_6H_4(NO_2)CH_3$-o.

the melting point (Figs. 1-4) with change in the dipole moments of molecules. In the transition of the m- and p-nitroanilines into the corresponding nitrodimethylanilines, the same change (both qualitatively and quantitatively) in the values of all of the properties is observed as for the nitrophenols when they are converted into the corresponding methyl ethers [1].

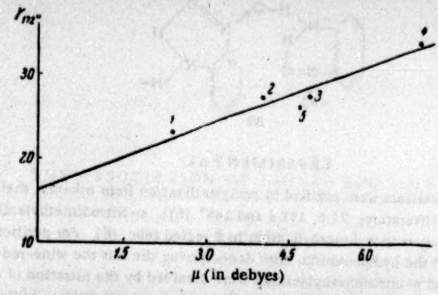


Fig. 3. Relationship between surface tension and dipole moment at 172°.

1 — $C_6H_4(COOC_2H_5)OH$-o, 2 — $C_6H_4(NO_2)N(CH_3)_2$-o, 3 — $C_6H_4(NO_2)N(CH_3)_2$-m, 4 — $C_6H_4(NO_2)N(CH_3)_2$-p 5 — $C_6H_4(NO_2)OC_2H_5$-p.

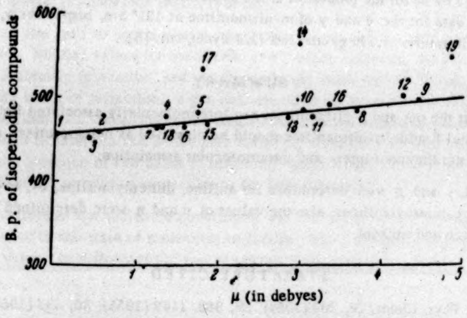
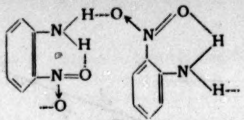


Fig. 4. Relationship between the boiling points of isoperiodic compounds and the dipole moment.

1 — $C_6H_4(C_2H_5)_2$-p, 2 — $C_6H_4(C_2H_5)_2$-o, 3 — $C_6H_5C_4H_9$-n, 4 — $C_6H_4(OCH_3)_2$-o, 5 — $C_6H_4(OCH_3)_2$-p, 6 — $C_6H_5OCOCH_3$, 7 — $C_6H_5OC_3H_7$ — n, 8 — $C_6H_4(CH_3)NO_2$-o, 9 — $C_6H_4(CH_3)NO_2$-p, 10 — $C_6H_5COC_2H_5$, 11 — $C_6H_4(NO_2)OH$-o, 12 — $C_6H_4(CHO)OCH_3$-o, 13 — $C_6H_4(COCH_3)OH$-o. 14 — $C_6H_4(COCH_3)OH$-m 15 — $C_6H_5COOCH_3$, 16 — $C_6H_5CH_2NO_2$, 17 — $C_6H_5CH_2COOH$, 18 — $C_6H_4(CH_3)OC_2H_5$-m 19 — $C_6H_4(NO_2)NH_2$-m

However, substantial differences are also observed between the nitroanilines and the nitrophenols in the relationship of some of the property values of the isomers, and specifically: a nearness in the values of the physical properties of the m- and o-nitroanilines and a sharp reduction in the values of these properties for the o-nitroaniline when it is converted to the o-nitrodimethylaniline, in magnitude coinciding with those for its isomers. These relationships are absent for the nitrophenols, where the meta isomer in its properties lies close to the p-, and not the o-nitrophenol; in the transition of o-nitrophenol to the methyl ether it is not a reduction that is observed, but even an increase in the values of γ and η. Apparently, o-nitroaniline should also be regarded as being an intermolecularly associated compound, further evidence of which is the fact that it, like its isomers, deviates sharply from a straight line in the isoperiodic series of compounds (Figs. 1 and 2). Evidently, o-nitroaniline should be regarded as being a mixed associated compound of the (II) type.



(II)

EXPERIMENTAL

The o-, m- and p-nitroanilines were purified by recrystallization from ethanol; their respective melting points were 71, 113 and 146° (literature: 71.5, 111.8 and 148° [5]). o-Nitrodimethylaniline was obtained from o-nitrochlorobenzene by heating it with dimethylaniline in a sealed tube [6]. For purification reasons the obtained amine was converted to the hydrochloride; after decomposing the salt the wine-red liquid was repeatedly vacuum-distilled. The m- and p-nitrodimethylanilines were obtained by the nitration of dimethylaniline [7]; after recrystallization from ethanol the first compound was obtained as long yellow needles with m.p. 61°, and the second as light yellow needles with a steel lustre and m.p. 162-163°. The aniline, dimethylaniline and o-, m- and p-toluidines were purified by repeated distillation.

The method of determining the values of the properties given in the tables was described earlier [1]. The values of d, γ and η for o-nitroaniline and the three nitrodimethylaniline isomers (if the value of d at 20° for the ortho isomer is neglected), and the value of η for the m- and p-nitroanilines, were determined for the first time. The values obtained by us for the properties of the remaining substances almost coincide with the literature values (for example, our data for the d and γ of m-nitroaniline at 131° are, respectively, 1.208 g/cm^3 and 41.8 dynes/cm, and from the literature: 1.199 g/cm^3 and 41.9 dynes/cm [8].

SUMMARY

1. It was shown that the m- and p-nitroanilines are intermolecularly associated liquids, while the nitrodimethylanilines are normal liquids; o-nitroaniline should be classified as being a mixed associated liquid, the molecules of which show simultaneous inter- and intramolecular association.

2. The values of d, γ and η were determined for aniline, dimethylaniline, o-, m- and p-nitroanilines, the toluidines and the nitrodimethylanilines; also the values of d and η were determined for the solutions of these compounds in benzene and ethanol.

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THE ASSOCIATION OF AMINES AND IMINES

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The criteria proposed for the association of liquids do not give a well defined answer to the question of whether the fatty and aromatic amines and imines show association or are normal. In different classifications of liquids the fatty amines and imines, similar to the alcohols, are classified as being associated liquids [1]. Some consider the fatty amines as also being associated in the vapor state [2]. However, the data for the infrared spectra [3] and the solubility of compounds of the type $CH(Hal)_3$ [4] in amines testify to the opposite – that the fatty amines and imines are normal in the liquid state. In addition, from the data, for example, for the parachor or dielectric permeability some authors [5] conclude that molecular association is present in the examined compounds, and others [6] conclude that it is absent.

The various criteria also lead to contradictory conclusions relative to the ability shown by aromatic amines and imines for association. Normal values for the Eötvös and Trouton constants, the data for the molecular weights and duration of dielectric relaxation, and obedience to the value $(\epsilon - n^2)^{1/2}$ (where ϵ is the dielectric permeability and $\underline{n}$ is the index of refraction), a general rule valid for unassociated substances, all testify that association is absent in aniline [7]. Meanwhile, the studies made of the infrared spectra of aniline, diphenylamine and other compounds in solutions and in the pure state [8] revealed a complete analogy in their behavior to that of the phenols: the presence of two bands in solutions, characteristic for monomeric and associated molecules, and only the bands of the associated molecules in the pure substances.

The contradictory nature of the indicated conclusions was evoked by a lack of foundation for part of the criteria given above relative to the state of molecules in liquids. Some of them (Trouton's constant, parachor, etc.) represent a partial value (or difference) of two or several properties of the same substance. Since the

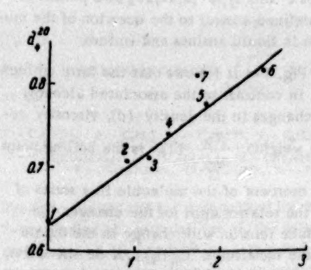

Fig. 1. Relationship between density and dipole moment.

1 — n-C_5H_{12}, 2 — $(C_2H_5)_2NH$, 3 — $(C_2H_5)_2O$, 4 — n-$C_4H_9NH_2$, 5 — n-C_4H_9F, 6 — n-C_3H_7CHO, 7 — n-C_4H_9OH.

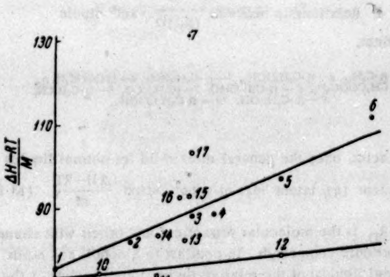

Fig. 2. Relationship between latent heat of vaporization and dipole moment.

1 — n-C_5H_{12}, 2 — $(C_2H_5)_2NH$, 3 — CH_3COOCH_3, 4 — $HCOOC_2H_5$, 5 — $CH_3COC_2H_5$, 6 — n-C_3H_7CN, 7 — n-C_4H_9OH, 8 — $C_6H_4(CH_3)_2$-p, 9 — $C_6H_4(CH_3)_2$-m, 10 — $C_6H_4(CH_3)_2$-o, 11 — $C_6H_5OCH_3$, 12 — C_6H_5CHO, 13 — $C_6H_4(NH_2)CH_3$-o, 14 — $C_6H_4(NH_2)CH_3$-p, 15 — $C_6H_5NHCH_3$, 16 — $C_6H_4(CH_3)OH$-m, 17 — $C_6H_5CH_2OH$.

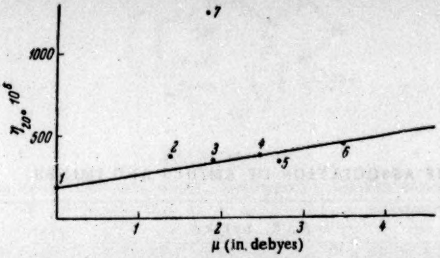

Fig. 3. Relationship between viscosity and dipole moment.

1 – n-C_4H_{10}, 2 – n-$C_3H_7NH_2$, 3 – $HCOOCH_3$, 4 – C_2H_5CHO, 5 – CH_3COCH_3, 6 – C_2H_5CN, 7 – CH_3COOH.

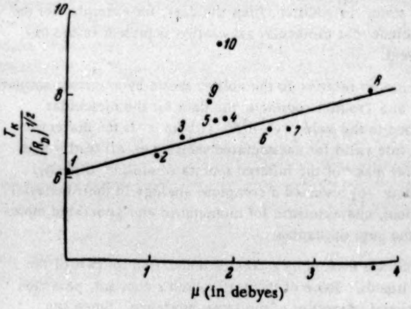

Fig. 4. Relationship between $\frac{T_k}{(R_D)^{1/2}}$ and dipole moment.

1 – n-C_6H_{14}, 2 – n-$C_4H_9OCH_3$, 3 – n-$C_5H_{11}NH_2$, 4 – $HCOOC_3H_7$ n., 5 – $CH_3COOC_2H_5$, 6 – n-C_3H_7CHO, 7 – $(C_2H_5)_2CO$, 8 – n-C_4H_9CN, 9 – n.-$C_5H_{11}OH$, 10 – n-C_3H_7COOH.

formation of complexes can exert an influence on all of the considered properties of a substance, a partial value (or difference), due to compensation in a number of cases, can fail to show up any anomaly. On the other hand, most of the existing criteria do not take into account that any anomaly (deviation from an established rule) can also arise as the result of other factors, and not only because of association. Only the relationships between the values of the properties of the macrosubstance and its component microparticles can serve as actual criteria for the state of a liquid. Associated liquids, whose properties are determined not by the properties of its molecules, but by the complexes of the latter, should not obey the indicated type of relationships valid for normal liquids, whose properties are determined by the properties of the individual molecules. Relationships of this type [9,12,13] also permit giving a well-defined answer to the question of the molecular state in liquid amines and imines.

From Fig. 1-4 it follows that the fatty amines and imines, in contrast to the associated alcohols and acids, obey the general rules valid for normal liquids relative to the changes in the density (d), viscosity coefficient (η), latent heat of vaporization $\frac{\Delta H - RT}{M}$ (M is the molecular weight), $\frac{T_k}{R_D^{1/2}}$ (T_k is the boiling point and R_D is the molecular refraction) and others with change in the dipole moment of the molecule in a series of isoperiodic compounds. In contrast to alcohols and acids, they also obey the relationships for the changes (in normal liquids) of the relative thermal coefficients of the density and surface tension with change in the dipole moment of the molecule [10]. They also behave like normal liquids in the substituted $C_nH_{2n+1}X$ or ArX series, obeying the general relationship for the changes of $\frac{T_k}{R_D^{1/2}}$ (Fig. 5), $\frac{\gamma v_M^{2/3}}{R_D}$ (v_M is the size of the molecule) [9] with change in the dipole moment of the molecule.

The fatty amines and imines also behave like normal liquids in the isologous series. Thus, if the alcohols show a noticeably higher T_k than do their isologs (the thio- and seleno-alcohols), then on the contrary, the

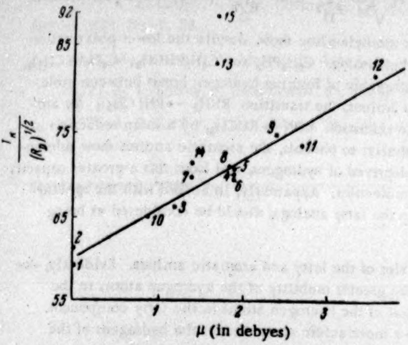

Fig. 5. Relationship between $\frac{T_k}{(R_D)^{1/2}}$ and dipole moment.

1 — $n\text{-}C_4H_9CH{=}CH_2$, 2 — $n\text{-}C_4H_9CH_3$, 3 — $n\text{-}C_4H_9OCH_3$, 4 — $n\text{-}C_4H_9Cl$,
5 — $n\text{-}C_4H_9Br$, 6 — $n\text{-}C_4H_9I$, 7 — $n\text{-}C_4H_9SH$, 8 — $n\text{-}C_4H_9OCOCH_3$,
9 — $n\text{-}C_4H_9CHO$, 10 — $n\text{-}C_4H_9OC_4H_9\text{-}n$, 11 — $n\text{-}C_4H_9COCH_3$,
12 — $n\text{-}C_4H_9CN$, 13 — $n\text{-}C_4H_9OH$, 14 — $n\text{-}C_4H_9NH_2$, 15 — $n\text{-}C_4H_9COOH$.

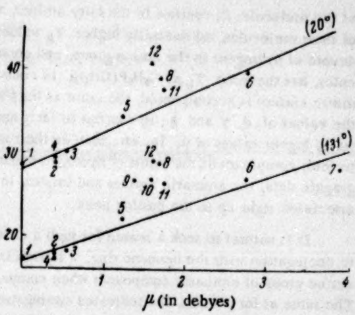

Fig. 6. Relationship between surface tension and dipole moment.

1 — $C_6H_4(CH_3)_2\text{-}p$, 2 — $C_6H_4(CH_3)_2\text{-}m$, 3 — $C_6H_4(CH_3)_2\text{-}o$, 4 — $C_6H_5C_2H_5$,
5 — $C_6H_5OCH_3$, 6 — C_6H_5CHO, 7 — C_6H_5CN, 8 — $C_6H_5CH_2OH$,
9 — $C_6H_4(OH)CH_3\text{-}o$, 10 — $C_6H_4(OH)CH_3\text{-}p$, 11 — $C_6H_5NHCH_3$,
12 — $C_6H_4(CH_3)NH_2\text{-}o$.

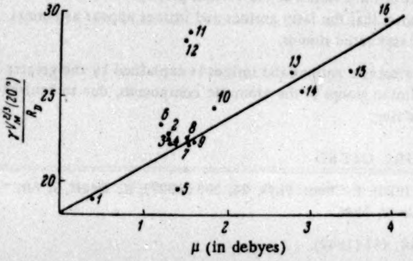

Fig. 7. Relationship between $\frac{\gamma V_M^{2/3}}{R_D}$ and dipole moment at 20°.

1 — $C_6H_5CH_3$, 2 — C_6H_5I, 3 — C_6H_5SH, 4 — $C_6H_5CH_2SH$, 5 — C_6H_5F,
6 — $C_6H_5OCH_3$, 7 — C_6H_5Cl, 8 — C_6H_5Br, 9 — $C_6H_5N(CH_3)_2$,
10 — $C_6H_5COOCH_3$, 11 — C_6H_5OH, 12 — $C_6H_5NH_2$, 13 — C_6H_5CHO,
14 — $C_6H_5COCH_3$, 15 — C_6H_5CN, 16 — $C_6H_5NO_2$.

amines and imines show a lower T_k than do their isologs – the phosphines and arsines. Replacement of hydrogen in the amino group, and especially in the imino group, by an alkyl produces in them nearly the same change in the values of the properties as does a corresponding lengthening of the hydrocarbon chain. Thus,

$$\frac{T_{k(C_2H_5)_2NH} - T_{k(C_2H_5)_3N}}{T_{k(C_2H_5)_2NH} - T_{k(n\text{-}C_3H_7)_2NH}} \doteq 0.6,$$

while for hydrocarbons:

$$\frac{T_{k(C_2H_5)_2CH_2} - T_{k(C_2H_5)_3CH}}{T_{k(C_2H_5)_2CH_2} - T_{k(n\text{-}C_3H_7)_2CH_2}} = 0.8.$$

As a result, the fatty amines and imines, in accord with the spectrographic data, behave like normal liquids whose properties under these thermodynamic conditions are determined by the properties of their molecules. This also follows from the results of the x-ray studies of methylamine in the solid state [11]. The values obtained for the distance N . . . . N of various molecules (3.18 and 3.27 A) coincide with the sum of the van der Waals radii for the two nitrogens, and consequently indicate the absence of an intermolecular hydrogen bond, the presence of which assumes some overlapping of the electron clouds of the atoms drawn together by the protonic (hydrogen) bond [12].

In contrast to the fatty analogs, the aromatic amines and imines show anomalous behavior similar to the phenols and alcohols. Thus, in isoperiodic series of compounds the aromatic amines and imines, in some cases even to a greater degree than the phenols and alcohols, deviate from the straight line that expresses the relationship between the values $\frac{\Delta H - RT}{M}$ (Fig. 2), γ (Fig. 6), T_k and η as a function of the dipole moment of the molecule [9,13]; thus, as do the phenols, aniline shows in the substituted series a sharp deviation from the straight line that expresses the dependence of $\frac{\gamma v_M^{2/3}}{R_D}$ (Fig. 7), $\frac{\eta}{\sqrt{M} \cdot R_D^{3/2}}$ and $\frac{T_k}{R_D^{1/2}}$ [9] on the dipole moment of the molecule; in contrast to the fatty amines, aniline and methylaniline show, despite the lower polarization of their molecules, substantially higher T_k values than do their isologs $C_6H_5PH_2$ and $C_6H_5PHCH_3$; $C_6H_5N(CH_3)_2$, devoid of hydrogens in the amino group, and consequently incapable of forming hydrogen bonds between molecules, has the same T_k as $C_6H_5P(CH_3)_2$. In contrast to fatty amines, the transition $RNH_2 \rightarrow RN(CH_3)_2$ for aromatic amines is accompanied, the same as for phenols in the transition $ROH \rightarrow ROCH_3$, by a sharp reduction in the values of d, γ and η; in contrast to fatty amines and similar to phenols, the aromatic amines show substantially higher values of d, T_k, etc., than do their metamers, deprived of hydrogens, and from this a greater capacity to form complexes as the result of hydrogen bonds between molecules. Apparently, in accord with the spectrographic data, the aromatic amines and imines, in contrast to the fatty analogs, should be considered as being associated right up to the boiling point.

It is natural to seek a reason for such a different behavior of the fatty and aromatic amines. Evidently, due to conjugation with the benzene ring, it is associated with the greater mobility of the hydrogen atoms in the amino group of aromatic compounds when compared with that of the hydrogen atoms in the fatty compounds. The same as for phenols, the indicated conjugation leads to a more acidic character for the hydrogens of the amino group, which favors an increase in the tendency to form intermolecular hydrogen bonds. Together with this, the presence of association for aromatic amines and imines shows that conjugation of the amino group with the ring does not substantially reduce (Buswell [7]) the capacity of the nitrogen to function as an electron donor.

SUMMARY

1. Only the relationships between the values of the properties of macrosubstances and those of their component microparticles can serve as well-defined criteria of the molecular state in liquids.

2. On the basis of the relationships established between the values of the various properties of macrosubstances and the properties of their molecules it was shown that the fatty amines and imines appear as normal liquids, while the aromatic amines and imines appear as associated liquids.

3. The difference in behavior shown by fatty and aromatic amines and imines is explained by the greater mobility of the hydrogen atoms found in the amino and imino groups of the aromatic compounds, due to conjugation of these groups with the double bonds of the benzene ring.

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REACTION MECHANISM FOR THE HYDROLYSIS OF SUCROSE

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The kinetics for the hydrolysis of sucrose in the presence of acid has been repeatedly studied by many investigators, beginning with the classic studies of Wilhelmy [1] and Arrhenius [2]. However, despite the large number of studies devoted to the kinetics of this reaction, its mechanism has not been fully established. This is associated both with a complexity of the hydrolysis itself and with the absence of a number of data, necessary for determination of the reaction scheme.

In the present investigation we made an attempt to discover the probable reaction scheme on the basis of studying the changes in the velocity constant of the reaction as a function of change in the sucrose and catalyst (hydrochloric acid) concentrations. In the calculations we used both our own measurements of the velocity constant and the data of a number of authors, who had studied the kinetics of this reaction using various methods: polarimetrically [3,6,7,8], dilatometrically [4] and calorimetrically [5].

EXPERIMENTAL

The polarimetric method was used to study the hydrolysis kinetics of sucrose in the presence of hydrochloric acid at 25°. The velocity constant was calculated graphically – from the value of the tangent slope of the linear function $\log(\alpha_t - \alpha_\infty)$ versus time, where α is the angle of rotation in the plane of polarization of the solution, which is equivalent to calculation by the formula for a monomolecular reaction $K_e = \frac{1}{t} \log \frac{C_0}{C}$ min^{-1}.

When the polarimetric method is used to measure the velocity constants for the hydrolysis of sucrose, great difficulty is encountered in determining the final angle of rotation. Due to the mutarotation of glucose and fructose (see [8]) the final angle of rotation changes with time; consequently, running the experiment for a long time, which is necessary to achieve practically complete hydrolysis of the sucrose in the presence of small amounts of acid, can lead to errors in determining the final angle of rotation. Heating of the solution to accelerate reaction can also lead to errors, since temperature exerts a variable influence on the change in the values of the velocity constants for the mutarotation of glucose and fructose. As was established by us, the final angle of rotation for the inverted sugar passes through a minimum (Table 1).

Consequently, for the final angle of rotation we took the minimum value of the angle of rotation from a series of experiments that were run in the same solvent and with the same sucrose content, but with different concentrations of acid. Observations revealed that solutions with an acid concentration of about 0.5 N (most sloping minimum) are best suited for determining the final angle of rotation. In solutions with a small acid content the reaction is slightly too slow at 25°, while with a higher acid content the change in the final angle of rotation is slightly too rapid.

Our measurement results for the velocity constants in water solutions are compared in Table 2 with the data obtained by other authors. In the first two columns of Table 2 are placed the values of the volume concentrations of acid (C_{HCl}) and sugar (C_s), and in the next column the values of the experimental velocity constants K_e, in reciprocal minutes, referred to unit concentration of acid and multiplied by the concentration of water in the solution. The references to the literature are given in the last column, in which connection our measurement results are designated by an asterisk.

Our measurement results for the velocity constants in alcohol-water solutions are given in Table 3. The amount of alcohol (wt. %) in the solvent water-alcohol is shown in the column "amount of alcohol in solvent".

TABLE 1

Amount			•		
of alcohol in the solvent (in wt. %)	of HCl (M/1000 g solvent)	of sucrose (in wt. % on the total amount of solvent)	initial	final (after 1-2 days)	after long standing (for 100-125 days)
0	1.5	10	206.03	170.62	172.51
10	1.0	10	207.10	171.87	173.20
10	1.5	10	206.34	171.47	173.51
20	1.0	10	206.19	172.72	173.95
20	1.5	10	205.53	172.23	174.61
50	0.5	10	205.33	175.45	176.12
50	1.0	10	204.76	175.00	177.17
0	0.5	20	236.90	161.87	162.87
0	1.0	20	236.42	161.48	163.57
0	1.5	20	234.86	160.40	171.64
10	0.5	20	256.42	163.63	164.85
10	1.0	20	235.19	162.73	165.60
10	1.5	20	234.43	162.10	166.40

TABLE 2

C_{HCl}	C_s	$\frac{K_e \cdot 10^3 \cdot C_{H_2O}}{C_{HCl}}$	Literature	C_{HCl}	C_s	$\frac{K_e \cdot 10^3 \cdot C_{H_2O}}{C_{HCl}}$	Literature
0.01	0.293	16.3	[5]	0.5	0.293	22.7	[1]
0.02	0.484	16.8	[7]		0.440	21.0	[2]
	1.010	18.4			0.293	22.4	[5]
0.1	0.293	18.4	[6]	0.531	0.108	23.3	[4]
	0.585	19.2		0.546	0.099	23.5	
	0.877	19.6		0.563	0.124	23.7	
	1.169	19.8		0.775	1.01	28.1	•
	1.460	19.7		0.877	0.121	27.1	[4]
	1.755	19.4		0.855	0.648	30.2	•
	2.047	18.6		0.906	0.115	27.1	[4]
0.1	0.293	18.5	[5]	0.928	0.309	30.4	•
0.095	0.147	18.6	[3]	0.952	0.293	28.4	[3]
0.095	0.293	18.0		0.972	0.147	27.8	
0.174	0.640	21.3	•	1.0	0.293	29.6	[5]
0.187	0.306	21.0		1.27	0.093	32.0	[3]
0.394	1.00	23.0		1.35	0.310	37.4	•
0.396	0.115	22.4	[4)	1.67	0.654	41.5	
0.43	0.640	24.6	•	1.80	0.314	39.6	
0.465	0.308	24.0		2.0	0.293	44.7	[5]
0.486	0.147	22.2	[3]	4.0	0.293	118	
0.486	0.293	22.9					

DISCUSSION OF RESULTS

The determinations of the velocity constants for the hydrolysis of sucrose at 25° in the presence of various amounts of hydrochloric acid and with various initial concentrations of the sugar (Table 2) reveal that the value $\frac{K_e}{C_{HCl}} \cdot C_{H_2O}$, within the limits of measurement error, at constant acid concentration, is constant and does not depend on the initial sugar concentration, but does increase with increase in the acid content. The dependence of this value on the acid concentration can be expressed by the approximate (average error 4%, maximum 12%) empirical equation:

$$\frac{K_e \cdot C_{H_2O}}{C_{HCl}} = 0.182 \cdot 10^{0.200 \cdot a_{HCl}}. \qquad (1)$$

The sugar and the water show stoichiometric participation in the pseudomonomolecular reaction for the hydrolysis of sucrose. However, the catalytic influence of the acid indicates that either an oxonium ion or a hydrogen ion participates in one of the intermediate stages of the reaction. Proceeding from this, the reaction for the hydrolysis can be depicted by one of the following schemes:

I a) $C_{12}H_{22}O_{11} + H_3O^+ \longrightarrow X^+$
$X^+ \rightleftharpoons 2C_6H_{12}O_6 + H^+$
$H^+ + H_2O \rightleftharpoons H_3O^+$;

b) $C_{12}H_{22}O_{11} + H_3O^+ \rightleftharpoons X^+$
$X^+ \longrightarrow 2C_6H_{12}O_6 + H^+$
$H^+ + H_2O \longrightarrow H_3O^+$.

II a) $C_{12}H_{22}O_{11} + H_2O \rightleftharpoons C_{12}H_{22}O_{11} \cdot H_2C$
$H_3O^+ \rightleftharpoons H^+ + H_2O$
$C_{12}H_{22}O_{11} \cdot H_2O + H^+ \longrightarrow X^+$
$X^+ \rightleftharpoons 2C_6H_{12}O_6 + H^+$;

b) $C_{12}H_{22}O_{11} + H_2O \rightleftharpoons C_{12}H_{22}O_{11} \cdot H_2O$
$H_3O \rightleftharpoons H^+ + H_2O$
$C_{12}H_{22}O_{11} \cdot H_2O + H^+ \rightleftharpoons X^+$
$X^+ \longrightarrow 2C_6H_{12}O_6 + H^+$.

The very slow stage of the reaction is shown by an arrow, while the sign of reversibility indicates a rapidly progressing stage.

Of the reaction schemes given above the one that is in closes agreement with experimental facts is Scheme IIa. In this case the kinetics equation for the reaction will be

$$-\frac{dC_s}{dt} = K_0 \cdot C_s \cdot C_{H^+}$$

$$\text{and } 2.3 \cdot K_e = -\frac{dC_s}{dt} \cdot \frac{1}{C_s} = K_0 \cdot C_{H^+} = K_0 \cdot K \frac{C_{H_3O^+}}{C_{H_2O}} \cdot \frac{f_{H_3O^+}}{f_{H^+} \cdot f_{H_2O}}, \qquad (2)$$

$$\text{since} \quad K_e = \frac{1}{t} \log \frac{C_0}{C_s} = \frac{1}{t \cdot 2.3} \ln \frac{C_0}{C_s} = -\frac{1}{2.3} \cdot \frac{dC_s}{dt} \cdot \frac{1}{C_s}.$$

Here K is the equilibrium dissociation constant of the oxonium ion, equal to $K = \frac{a_{H^+} \cdot a_{H_2O}}{a_{H_3O^+}}$, and $f_{H_3O^+}$, f_{H^+}, and f_{H_2O} are the stoichiometric (volume) activity coefficients of the oxonium, hydrogen and water ions, respectively.

In water solutions in the presence of acid the equilibrium of the dissociation $H_3O^+ \rightleftharpoons H^+ + H_2O$ is shifted to the side of forming the oxonium ion, and $C_{HCl} \simeq C_{H_3O^+}$

Then from Equation (2) it follows that

$$\frac{K_e \cdot C_{H_2O}}{C_{HCl}} = \frac{K_0 \cdot K}{2.3} \cdot \frac{f_{H_3O^+}}{f_{H^+} \cdot f_{H_2O}}. \qquad (3)$$

We will check to what degree Equation (3) is in accord with the empirical Equation (1). The activity coefficient of water at 25° in hydrogen chloride solutions is linked with the concentration of the latter by the following empirical equation (with an error of up to 2%, in the HCl concentration limits of 0-4 N).

$$f_{H_2O} = 10^{-0.0175 \cdot c_{HCl}}. \tag{4}$$

From the Brõnsted equation

$$\log \frac{f_{H_3O^+}}{f_{H^+}} = A \cdot B \cdot \mu \left(a^0_{H_3O^+} - a^0_{H^+}\right), \tag{5}$$

where μ is the ionic strength, $\mu = C_{HCl}$, A = 0.507, B = 0.329 [9], a^0 is the ionic radius.

As a first approximation we will substitute $a^0_{H_3O^+} - a^0_{H^+} = r_{H_2O}$, i.e. the radius of the water molecule. Taking for the latter (from the values of the refraction and of the constant in the van der Waals equation) $r_{H_2O} = 1.11$ A, from Equations (4) and (5) we obtain:

$$\frac{f_{H_3O^+}}{f_{H^+} \cdot f_{H_2O}} = 10^{0.203 \cdot c_{HCl}}$$

and

$$\frac{K_e \cdot C_{H_2O}}{C_{HCl}} = \frac{K_0 \cdot K}{2.3} \cdot 10^{0.203 \cdot c_{HCl}}.$$

A comparison of the obtained equation with the empirical Equation (1) reveals not only their completely quantitative agreement, but also an agreement of the values of the factor, dependent on the hydrochloric acid concentration.

The other possible reaction schemes are found to be in contradiction of experimental fact.

Thus, for example, Scheme Ia requires that the value $\frac{K_e}{C_{HCl}}$ be independent of the acid concentration. In such case $\frac{dC_s}{dt} = K_0 \cdot C_s \cdot C_{H_3O^+}$ and $\frac{K_e}{C_{HCl}} = K_0 = \text{const}$. In the case of the reaction proceeding in accord with Scheme Ib:

$$-\frac{dC_s}{dt} = K_0 \cdot C_{X^+} = K_0 \cdot K' \cdot C_s \cdot C_{H_3O^+} \cdot \frac{f_s \cdot f_{H_3O^+}}{f_{X^+}}.$$

The activity coefficient of the sugar at zero sugar concentrations is $f_s = 1$ and $\frac{K_e}{C_{HCl}} \simeq K \cdot K' \cdot \frac{f_{H_3O^+}}{f_{X^+}}$. This value should decrease with increase in the ionic strength. From the Brõnsted equation

$$\log \frac{f_{H_3O^+}}{f_{X^+}} = A \cdot B \cdot \mu \left(a^0_{H_3O^+} - a^0_{X^+}\right).$$

Since $a^0_{X^+} > a^0_{H_3O^+}$, then $\frac{f_{H_3O^+}}{f_{X^+}}$ should decrease with increase in acid concentration. The same should be observed for variants IIb and IIIb.

Scheme IIa leads to the relationship:

$$\frac{K_e}{C_{HCl}} = K'' \cdot \frac{f_s \cdot f_{H_3O^+}}{f_{H^+} \cdot f_{C_{12}H_{22}O_{11} \cdot H_2O}}. \tag{6}$$

When $C_{HCl} = 0$ $\frac{f_{H_3O^+}}{f_{H^+}} = 1$, and from Equations (3) and (6) it follows:

$$\frac{f_s \cdot C_{H_2O}}{f_{C_{12}H_{22}O_{11} \cdot H_2O}} = \text{const.} \tag{7}$$

From the data given by Harned [9] for the osmotic coefficients of aqueous sugar solutions, we calculated the activity coefficients of the water in these solutions. In aqueous sugar solutions at 25°, up to a sugar concentration of 2.3 M, and with an error of up to 3%

$$C_{H_2O} = 55.5 - 12 \cdot C_s \text{ and } \log f_{H_2O} = 0.104 \cdot C_s = 0.48 - 0.087 \cdot C_{H_2O}.$$

Here f_{H_2O} is the stoichiometric activity coefficient of water:

$$f_{H_2O} = \frac{P_{H_2O}}{P^0_{H_2O}} \cdot \frac{55.5}{C_{H_2O}} = \frac{a_{H_2O}}{C_{H_2O}}.$$

Calculation reveals that the activity of water a_{H_2O} in aqueous sugar solutions is practically constant up to a sugar concentration of 1.0 M and is equal to 55.5 ± 0.1, with a slight decrease (to 51.0) when the sugar concentration is increased to 2.0 M.

In accord with Scheme IIa:

$$\frac{a_{C_{12}H_{22}O_{11} \cdot H_2O}}{a_{H_2O} \cdot a_s} = K'''. \tag{8}$$

Equations (7) and (8) under the condition a_{H_2O} = const. lead to a relationship that is contradictory to the reaction scheme:

$$\frac{C_{C_{12}H_{22}O_{11} \cdot H_2O} \cdot C_{H_2O}}{C_s} = \text{const.}$$

That the proposed scheme for the hydrolysis of sucrose is in agreement with the experimental data is also supported by the experiments run in alcohol-water solutions (Table 3), where $C_{HCl} \simeq C_{H_3O^+} + C_{C_2H_5OH_2}$ and

$$\frac{K_e}{C_{HCl}} = \frac{K_e}{C_{H_3O^+} + C_{C_2H_5OH_2^+}} = \frac{K_0 \cdot C_{H^+}}{2.3\left(\frac{a_{H^+} \cdot a_{H_2O}}{f_{H_3O^+} \cdot K} + \frac{a_{H^+} \cdot a_{alc.}}{f_{C_2H_5OH_2^+} \cdot K_1}\right)}.$$

Here K_1 is the dissociation constant of the ethoxonium ion, where $K_1 = \frac{a_{H^+} \cdot a_{alc}}{a_{C_2H_5OH^+}}$, a_{alc} is the activity of the alcohol, and $f_{C_2H_5OH_2^+}$ is the activity coefficient of the ethoxonium ion.

At $C_{HCl} = 0$ and taking into consideration Equations (1) and (2)

$$\frac{K_e}{C_{HCl}} = \frac{0.182}{C_{H_2O} \cdot \frac{f_{H^+} \cdot f_{H_2O}}{f_{H_3O^+}} + \frac{K}{K_1} \cdot C_{alc} \cdot \frac{f_{H^+} \cdot f_{alc}}{f_{C_2H\,OH^+}}}.$$

TABLE 3

Amount of alcohol in solvent (in wt. %)	c_{HCl}	c_s	$K_e \cdot 10^4$	$\frac{K_e \cdot c_{H_2O}}{c_{HCl}}$	$\frac{K}{K_1}$
10	0	0.300	—	0.148	5.3
	0.09	0.300	3.07		
	0.019	0.304	7.20		
	0.46	0.306	20.7		
	0.91	0.306	53.8		
	1.35	0.308	104.7		
20	0	0.297	—	0.118	5.5
	0.046	0.297	1.45		
	0.183	0.297	6.55		
	0.452	0.300	19.3		
	0.895	0.300	51.5		
	1.32	0.304	96.5		
	1.75	0.306	143		
50	0	0.281	—	0.0455	7.7
	0.043	0.281	0.83		
	0.0865	0.281	1.77		
	0.175	0.282	4.88		
	0.43	0.283	16.86		
	0.845	0.286	46.25		
10	0	0.626	—	0.140	6.9
	0.086	0.630	3.11		
	0.172	0.630	6.54		
	0.425	0.635	20.4		
	0.875	0.632	52.7		
	1.25	0.645	99.07		
20	0	0.620	—	0.114	6.1
	0.42	0.625	16.9		
	0.83	0.627	41.7		
	1.23	0.630	76.13		
50	0	0.585	—	0.0468	7.1
	0.40	0.592	14.0		
	0.785	0.596	38.2		
	1.18	0.600	71.8		
	1.535	0.602	114.15		
20	0	0.980	—	0.115	5.9
	0.38	0.980	18.0		
	0.757	0.980	46.3		
30	0	0.970	—	0.0868	6.5
	0.38	0.970	16.3		
	0.75	0.970	42.4		
50	0	0.940	—	0.0595	5.4
	0.08	0.940	3.75		
	0.367	0.940	15.5		
	0.725	0.940	39.9		

Since $\frac{K_e \cdot C_{H_2O}}{C_{HCl}}$ is independent of the sugar concentration in water solutions at constant acid concentration, it can be assumed that $\frac{f_{H^+} \cdot f_{H_2O}}{f_{H_3O^+}}$ and $\frac{f_{H^+} \cdot f_{alc}}{f_{C_2H_5OH_2^+}}$ at zero acid concentration are equal to unity.

Then

$$\frac{K_e : C_{H_2O}}{C_{HCl}} = \frac{0.182}{1 + \frac{K}{K_1} \cdot \frac{C_{alc}}{C_{H_2O}}} \text{ and } \frac{K}{K_1} = \left(\frac{0.182}{\frac{K_e \cdot C_{H_2O}}{C_{HCl}}} - 1 \right) \cdot \frac{C_{H_2O}}{C_{alc}}.$$

The values of $\frac{K_e \cdot C_{H_2O}}{C_{HCl}}$ for zero acid concentration are given in Table 3, as are also the ratios of the dissociation constants of the oxonium and ethoxonium ions, calculated from these values. From the data in Table 3 it can be seen that with a substantial change in the alcohol (from 10 to 50%) and sugar (from 0.28 to 0.98 mole/liter) concentrations the ratio K/K_1 remains practically constant, on the average being equal to 6.3 ± 0.7, with a relative error of 11% and a maximum error of 22%. As a result, the experimental data obtained for the alcohol-water solutions support the probability of the proposed scheme for the hydrolysis of sucrose.

SUMMARY

1. The velocity constants were determined for the hydrolysis of sucrose in water and alcohol-water solutions at 25° in the presence of various amounts of hydrochloric acid and the sugar.

2. On the basis of comparing the velocity constants obtained by various authors for the hydrolysis of sucrose the problem of the mechanism of the hydrolysis reaction was examined, and a probable scheme for the reaction was proposed.

3. Proceeding from the scheme proposed for the hydrolysis reaction, an attempt was made to approximately calculate the ratios of the dissociation constants of the oxonium and ethoxonium ions.

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ELECTROSYNTHESIS OF o- AND p-METHOXYPHENYLHYDRAZINES

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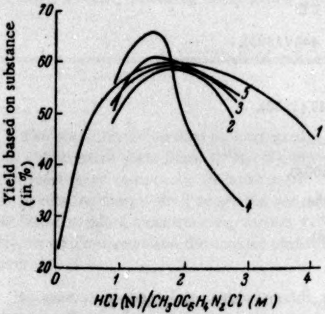
The arylhydrazines find much use in the synthesis of a number of important pyrazolones, used for the manufacture of dyes and medicinals. One of the principal methods of synthesizing arylhydrazines consists in the reduction of the corresponding diazo compounds. The chemical methods of reducing diazo compounds have been well studied and are extensively used in industry and in laboratories. At the same time the electrosynthesis of arylhydrazines has been studied very slightly. The principal studies in this direction have been devoted to the electrosynthesis of phenylhydrazine [1-3] and some of its derivatives [2,4-6].

Methods for the electrochemical preparation of methoxyphenylhydrazines are not described in the literature. Only brief statements exist in the literature relative to the chemical synthesis of these phenylhydrazine derivatives, in which connection the yields of methoxyphenylhydrazines do not exceed 50% [7].

We investigated the electroreduction of the o- and p-methoxyphenyldiazonium chlorides to the o- and p-methoxyphenylhydrazines, and studied the influence of the following factors on the yields (based on both the substance taken for reaction and on the current) of the o- and p-methoxyphenylhydrazines: concentration of hydrochloric acid, current density, and also the ratios between the HCl and diazonium salt concentrations.



Relationship between the yields of o- and p-methoxyphenylhydrazines and the ratios of the hydrochloric acid and diazonium salt concentrations.
Concentration of o-$CH_3OC_6H_4N_2Cl$: 1) 0.05 M, 2) 0.1 M, 3) 0.2 M.
Concentration of p-$CH_3OC_6H_4N_2Cl$: 4) 0.05 M, 5) 0.1 M.

Solutions with various concentrations of the methoxyphenyldiazonium chloride were studied: for the o-isomer – 0.05, 0.1 and 0.2 M, and for the p-isomer – 0.05 and 0.1 M. The influence of HCl concentration was studied in the interval 0.05-0.5 N for o-$CH_3OC_6H_4N_2Cl$ and 0.05-0.25 N for p-$CH_3OC_6H_4N_2Cl$. The influence of the current density was studied in the limits 1.25-7.5 amp/dm^2.

As a result of the experiments made it was established that the maximum yields of o-methoxyphenylhydrazine (60.6% based on substance and 45% based on current) can be obtained when the following optimum conditions are observed: concentration of o-methoxyphenyldiazonium chloride 0.1 M, concentration of HCl 0.15 N, and current density at the cathode 2.5 amp/dm^2.

The following conditions can be recommended for the electrosynthesis of p-methoxyphenylhydrazine, where the yield based on substance is 66.6%, and based on current is 44.4%: concentration of p-methoxyphenyldiazonium chloride 0.05 M, concentration of HCl 0.075 N, and current density at the cathode 5 amp/dm^2.

The results of the experiments on establishing the relationship between the yields of the o- and p-methoxyphenylhydrazines and the ratios of the hydrochloric acid and diazonium salt concentrations proved very interesting. The results of these experiments are shown in the figure.

From the plot it can be seen that the maxima of the curves, corresponding to the optimum yields of the methoxyphenylhydrazines, are found at definite ratios of the hydrochloric acid and diazonium salt concentrations. This ratio is: for the electroreduction of o-$CH_3OC_6H_4N_2Cl$ 1.8, and for the electroreduction of p-$CH_3OC_6H_4N_2Cl$ 1.5. When the indicated ratios are observed it is also possible to obtain good yields of the methoxyphenylhydrazines from more concentrated diazonium salt solutions. However, in such cases it is necessary to take measures to prevent tarring of the final product, which deposits as a solid from concentrated solutions. As our experiments revealed, beneficial results are obtained by saturating the catholyte and the area over it with carbon dioxide gas.

EXPERIMENTAL

Mercury,* serving as the cathode, was placed in the bottom of a 0.5 liter cylindrical beaker. A ceramic diaphragm with opening on the bottom was fastened in the beaker through a stopper. A glass tube was inserted through a hole in the stopper, through which descended a glass stirrer for mixing the catholyte. A graphite anode was placed inside the diaphragm. Besides the diazonium salt, the catholyte (100 ml) contained hydrochloric acid and potassium chloride (2 M). The presence of potassium chloride in the catholyte raises the electroconductivity and represses side reaction of the diazonium salt with the arylhydrazine [3]. The anolyte was 3 N H_2SO_4. To prevent decomposition of the diazonium salt, the catholyte temperature was maintained in the limits of -2 to $-6°$ by means of a cooling mixture.

Prior to each experiment the o- or p-methoxyphenyldiazonium salt was prepared from either o- or p-anisidine. The diazotization was run at a temperature of -5 to $-7°$.

To identify the methoxyphenylhydrazines the benzaldehyde methoxyphenylhydrazones with m.p. 171° were prepared. The amount of methoxyphenylhydrazine was determined by iodometric titration [3].

SUMMARY

1. A method was developed for the electrosynthesis of o- and p-methoxyphenylhydrazines by reduction of the corresponding diazonium salts.

2. Conditions were established for running the electroreductions, under which it is possible to obtain greater yields of the o- and p-methoxyphenylhydrazines than when chemical methods are used.

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*According to the literature [1-6], the arylhydrazines in general are either not formed or their yields are very small when other materials are used as the cathode.

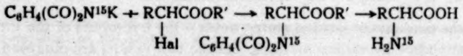
STUDIES OF COMPOUNDS LABELED WITH C^{14} AND N^{15}

V. SYNTHESIS OF α-N^{15}-AMINO ACIDS

V. I. Maimind, K. M. Ermolaev and M. M. Shemyakin

Various methods are described in the literature for the synthesis of amino acids labeled with heavy nitrogen in the α-position. The method most frequently used for their preparation was that of reductive amination [1], where the starting compounds are $N^{15}H_3$ and the corresponding keto acid; here, despite the necessity of using a large excess of $N^{15}H_3$, it was frequently possible to obtain the labeled amino acids in satisfactory yield due to recovery of the unreacted $N^{15}H_3$. Only N^{15}-glycine [1], α-N^{15}-lysine [2,3] and α-N^{15}-ornithine [4,5] were synthesized by the Gabriel phthalimide method; these acids were obtained by starting from potassium N^{15}-phthalimide and the esters of the corresponding α-bromo or α-chloro acids (at times CuO or KI were used as catalysts). It should be mentioned that N^{15}-glycine was also obtained by the reaction of $N^{15}H_4HCO_3$ with chloroacetic acid [6], and although the total yield of amino acid was only 8% (based on $N^{15}H_3$), still the loss of labeled ammonia was only 2%, since 90% of it could be recovered.

As the result of making a comparative study of various ways of synthesizing N^{15}-labeled α-amino acids, we decided that the Gabriel phthalimide method can be a general method for the synthesis of α-N^{15}-amino acids, in which connection we worked out the optimum conditions of this synthesis and, to a considerable degree, made each step universal, including the isolation and purification of the final labeled amino acids:



$$C_6H_4(CO)_2N^{15}K + \underset{\displaystyle Hal}{RCHCOOR'} \longrightarrow \underset{\displaystyle C_6H_4(CO)_2N^{15}}{RCHCOOR'} \longrightarrow \underset{\displaystyle H_2N^{15}}{RCHCOOH}$$

The phthalimide method permits starting from available potassium N^{15}-phthalimide, readily obtained in nearly quantitative yield from $N^{15}H_3$ [7]; the esters of the α-halo acids are also readily available, of which the bromo-substituted compounds are to be preferred. This method is extremely simple as regards execution technique, does not require complicated apparatus, and is characterized by great reliability. It makes it possible to obtain under fairly standard conditions the various N^{15}-labeled amino acids in consistently high yields and fairly high purity, in which connection the labeled phthalimide, at times formed as a secondary product, can be easily recovered.

In most cases the starting α-halo acids, needed for the synthesis of α-amino acids, are generally available substances. The more complex α-halo acids are most simply obtained from the corresponding unlabeled α-amino acids, replacing the amino group by a bromine atom (see [8]). In this way we obtained α-bromoisovaleric, α-bromo-β-phenylpropionic and α-bromo-β-(p-methoxyphenyl) propionic acids in 70-90% yield. With regard to the conversion of α-halo acids into esters, it is expedient to use diazomethane.

It proved most convenient to run the condensation of potassium phthalimide with the esters of α-bromo acids in the presence of dimethylformamide [9]. This permits not only a lower reaction temperature, a shorter heating time, and as a result, obtaining a purer condensation product, but frequently makes it possible to raise the yield.

Usually there is no need to isolate and purify the phthaloylamino acid esters obtained as the result of condensation, but at times (for example, in the synthesis of tyrosine) to obtain satisfactory yields in the hydrolysis step such purification is fully necessary, even though the yield of esters is lowered here. • In the condensation of some of the α-halo acid esters with potassium phthalimide considerable amounts of phthalimide are formed, the substantial reduction of which cannot be accomplished by modifying the condensation conditions (duration and temperature of reaction, extent to which the used reagents are purified and dried, presence or absence of a solvent). Apparently, this phenomenon is associated with the structure of the starting α-halo acid esters, which, under the influence of potassium phthalimide, are more or less capable of cleaving a molecule of hydrogen halide, as a result of which phthalimide is formed. From the data given in Table 1 it can be seen that substantial cleavage of hydrogen halide occurs only for the esters of those α-halide acids that contain alkyl or aryl radicals on the β-carbon atom. The cleavage of a small amount of HBr from the diethyl ester of α-bromoglutaric acid is probably conditioned by the influence of the γ-carboxyl group.

TABLE 1

Starting α-halo acid ester	Amount of phthalimide formed (in %)
$BrCH_2COOCH_3$	0
$CH_3CHBrCOOCH_3$	0
$C_6H_5CONHCH_2CH_2CH_2CHBrCOOCH_3$	0
$C_6H_4(CO)_2NCH_2CH_2CH_2CHBrCOOCH_3$	0
$C_6H_5CONHCH_2CH_2CH_2CH_2CHBrCOOC_2H_5$	0
$C_2H_5OOCCH_2CH_2CHBrCOOC_2H_5$	4
$(CH_3)_2CHCHClCOOCH_3$	25
p-$CH_3OC_6H_4CH_2CHBrCOOCH_3$	30
$C_6H_5CH_2CHBrCOOCH_3$	35
$(CH_3)_2CHCHBrCOOCH_3$	53

In connection with the above circumstances the greatest difficulties arose in the synthesis of valine. Here the best results were obtained by condensing potassium phthalimide with the methyl ester of α-bromoisovaleric acid in dimethylformamide at 120°, but even in this case more than 50% of phthalimide was formed. Attempts to reduce the phthalimide formation proved unsuccessful. Thus, with the esters of α-chloroisovaleric acid, the condensation in dimethylformamide went only at 140-145°, and without the solvent – at 220-230° (in sealed tubes), and although in this case the phthalimide formation was only 25%, at the same time the yield of the phthaloylvaline ester was also reduced. The situation was not improved by using the ureides of the α-bromo- and α-iodoisovaleric acids, or by using the isopropylbromomalonic ester instead of the α-haloisovaleric esters.

The second step in the synthesis of labeled amino acids – the hydrolysis of the esters of their N-phthaloyl derivatives – can be accomplished by various methods, but the best results are obtained by heating these esters with a mixture of acetic and hydrobromic acids with simultaneous removal by distillation of the readily volatile products formed. When pure esters of the phthaloyl derivatives were taken for hydrolysis the yield of the amino acid was 90-95% and higher. The described method was examined using various amounts of $N^{15}H_3$ – from 2 to 100 millimoles. The following labeled amino acids were synthesized with this method: •• glycine (95%), alanine (95%), valine (82%), glutamic acid (85%), ornithine (78%), lysine (68%) phenylalanine (86%) and tyrosine (71%).•••

•By means of special experiments, it was shown that in the case of tyrosine it is necessary to thoroughly purify the corresponding phthaloyl derivative from the p-methoxycinnamic acid ester, formed at the same time as the result of partial HBr cleavage from the starting α-bromo-β-(p-methoxyphenyl) propionic acid ester. This purification is necessary for the reason that, under the subsequent hydrolysis conditions, the p-methoxycinnamic acid ester is cleaved with the formation of anisaldehyde and p-hydroxybenzaldehyde. The latter give Schiff bases with the simultaneously formed amino acids, which then isomerize to pyrotartaric acid derivatives, in turn suffering a series of further changes (see [10]), which in the end leads to a marked reduction in the tyrosine yield and a sharp impairment in its quality.

••The yields of the amino acids are indicated in parentheses, based on the potassium N^{15}-phthalimide and taking into account the recovered phthalimide.

•••V. N. Zaitsev participated in working out the methods for the synthesis of N^{15}-valine and N^{15}-phenylalanine.

An attempt to synthesize the optically active phenylalanine from the ester of the corresponding α-halo acid led to obtaining only the racemate; racemization occurs at the step of condensing the ester with potassium phthalimide.

EXPERIMENTAL

1. Preparation of α-bromo acids and their esters from amino acids. A solution of 0.1 mole of the amino acid in 165 ml of 3 N H_2SO_4 was cooled to 0° and then 40 g of finely powdered KBr was added, with constant stirring. Then a saturated water solution of 9 g of $NaNO_2$ was added dropwise in 3-4 hours at −10°. After we added about 50 ml of water, the obtained α-bromo acid was either filtered (in the case of O-methyltyrosine)• or extracted with ether (in the case of phenylalanine and valine), after which it was purified either by recrystallization or by vacuum distillation. The yield of the α-bromo acids reaches 70-90%. To obtain the methyl esters, either a solution or a suspension of the α-bromo acid in ether was treated with a slight excess of diazomethane, dissolved in ether. After distillation of the ether the residue was thoroughly purified (Table 2). The yields of the esters were about 90%.

TABLE 2

α-Bromo acid ester	Method of purification	Constants	Br analysis (in %)	
			found	calc.
$C_6H_5CONH(CH_2)_3CHBrCOOCH_3$•	Washing with ether at −10°	m. p. 60—61°	25.70	25.42
$C_6H_4(CO)_2N(CH_2)_3CHBrCOOCH_3$••	Crystallization from ether	m. p. 61—62°	23.55	23.50
$C_6H_5CONH(CH_2)_4CHBrCOOCH_3$	Washing with ether at −10°	m. p. 43—44°	24.44	24.39
$EtOOCCH_2CH_2CHBrCOOEt$•••	Distillation	b. p. 132° (at 7 mm)	29.84	29.92
$C_6H_5CH_2CHBrCOOCH_3$	Distillation	b. p. 90° (at 0.05 mm)	33.15	32.83
$p\text{-}CH_3OC_6H_4CH_2CHBrCOOCH_3$	Distillation	b. p. 102° (at 0.03 mm)	29.05	29.27

•Obtained by treating the impure α-bromo-δ-benzoylaminovaleric acid with CH_2N_2 [13].

••For the synthesis of the starting acid see [14].

•••Obtained by the bromination of $C_2H_5OOC(CH_2)_3COCl$ [15] (b.p. 92° at 7 mm) at 90° for 4 hours and subsequent treatment with absolute alcohol.

2. Condensation of potassium N^{15}-phthalimide with esters of α-halo acids (Table 3). To 0.1 mole of potassium N^{15}-phthalimide, previously dried in vacuo (1 hour at 200° and 0.05 mm [16]), was added 0.1-0.13 mole of the α-halo acid ester and 40-60 ml of dry neutral dimethylformamide. Then, with frequent shaking, the mixture was heated until all of the potassium phthalimide crystals, which could easily be distinguished from the gradually deposited heavy precipitate of potassium bromide (or chloride), had dissolved. On conclusion of reaction, the obtained potassium bromide (or chloride) was filtered, washed with 10-15 ml of dimethylformamide, and the filtrate evaporated in vacuo, distilling off not only the dimethylformamide, but also unreacted α-halo acid ester, and at times also the formed ester of the α, β-unsaturated acid,•• in which connection the bath temperature should not exceed 120°. The residue was stirred with 60-80 ml of chloroform, the mixture cooled for

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•The starting O-methyltyrosine with m.p. 242° (from water) can be obtained from N-acetyl-O-methyltyrosine [11,12] by heating it with HCl (1:4) for 6 hours at 95-100°. The α-bromo-β-(p-methoxyphenyl) propionic acid, obtained from the O-methyltyrosine, has m.p. 119° (from dilute CH_3COOH). Found %: Br 31.06; CH_3O 11.63. $C_{10}H_{11}O_3Br$. Calculated %: Br 30.86; CH_3O 11.97.

••In the synthesis of tyrosine the ester of the corresponding α, β-unsaturated acid is separated by crystallization.

TABLE 3

Amino acid synthesized	Starting α-halo acid ester	Condensation			Condensation								Hydrolysis		
							phthaloylamino acid ester							amino acid (%)	
									analysis (in %)						
									found		calculated				
		amount of ester (in moles)	temperature	reaction time (hrs)	amount of recovered phthalimide (in %)	recrystallization	melting point	C	H	C	H	total reaction time (hrs)	por calc. recovered phthalimide	calc. with recovered phthalimide
N^{15}-Glycine	$BrCH_2COOCH_3$	0.110	60—70°	0.25	0	50% alcohol						10	95•	—
N^{15}-Alanine	$CH_3CHBrCOOCH_3$	0.110	70—80	0.5	0	50% alcohol	69°	61.83	4.85	61.80	4.75	10	95	—
N^{15}-Valine	$(CH_3)_2CHCHBrCOOCH_3$	0.130	118—122	0.5	53	50% alcohol	44	64.10	5.70	64.30	5.74	8	39	82
N^{15}-Glutamic acid	$C_2H_5OOC(CH_2)_2CHBrCOOC_2H_5$	0.110	95—100	1.5	4	—						8	81	85
α-N^{15}-Ornithine · HCl	$C_6H_4(CO)_2N(CH_2)_3CHBrCOOCH_3$	0.103	90—95	1.0	0	50% alcohol	134	64.99	4.47	65.17	4.72	24	78••	—
α-N^{15}-Lysine · HCl	$C_6H_5CONH(CH_2)_4CHBrCOOC_2H_5$	0.103	95—100	1.5	0	—						24	68•••	—
N^{15}-Phenylalanine	$C_6H_5CH_2CHBrCOOCH_3$	0.110	85—90	0.5	20	Ether	92	70.16	4.79	69.81	4.89	10	56	86
N^{15}-Tyrosine	p-$CH_3OC_6H_4CH_2CHBrCOOCH_3$	0.100	85—90	1.0	30	Alcohol	141	67.04	5.22	67.23	5.05	8	52	71

•The same results were obtained when the reaction was run with the ethyl ester of chloroacetic acid at 85-95°.

••The same results were obtained when the reaction was run under similar conditions with $C_6H_5CONH(CH_2)_3CHBrCOOCH_3$.

•••The same results were obtained when the reaction was run under similar conditions with $C_6H_5CONH(CH_2)_4CHBrCOOCH_3$.

TABLE 4

Amino acid	Amount of N^{15} in starting potassium phthalimide (in at%)	Final amino acid			
		Amount of N^{15} (in a %)		total amount of nitrogen (in %)	
		found	calc.	found	calc.
N^{15}-Glycine	21.3	21.2	21.3	18.60	18.86
N^{15}-Alanine	18.6	18.2	18.6	15.42	15.67
N^{15}-Valine	21.3	20.8	21.3	11.96	12.14
α-N^{15}-Ornithine · HCl	21.3	10.8	10.8	16.65	16.74
α-N^{15}-Lysine · HCl	21.3	10.8	10.8	15.64	15.42
N^{15}-Glutamic acid	21.3	21.3	21.3	9.55	9.63
N^{15}-Phenylalanine	21.3	20.9	21.3	8.67	8.58
N^{15}-Tyrosine	21.3	20.8	21.3	7.55	7.82

6-8 hours at 0°, the phthalimide precipitate and traces of inorganic salt separated, the precipitate washed with 10-15 ml of chloroform, and the solution evaporated in vacuo.

In the case of the phthaloylvaline ester the obtained residue was stirred again with 30-40 ml of chloroform, and after cooling for 2 hours at 0°, the deposited phthalimide was again separated.

In the preparation of the phthaloyltyrosine ester, in order to achieve more complete removal of the phthalimide, the chloroform solution, after filtration, was washed twice with 0.1 N NaOH solution (in 40 ml portions) and twice with water (also in 40 ml portions); acidification of the alkaline solution gave an additional 3-5% of phthalimide.

The isolated phthalimide was washed with water until it gave a negative test for halide ion, and then it was dried in a vacuum-desiccator. The phthaloylamino acid ester, obtained either in crystalline form or as an oil, was subjected to hydrolysis without further purification.

An exception is the methyl ester of N-phthaloyl-O-methyltyrosine, which should be recrystallized first from 100 ml, and then from 150 ml of alcohol; instead of a second recrystallization the residue can be triturated with isoamyl acetate.

3. Hydrolysis of phthaloylamino acid esters (Table 3). For the hydrolysis of most of the phthaloylamino acid esters, the residue after distillation of the chloroform obtained in Experiment 2, was stirred with 50 ml of glacial acetic acid and to the hot solution was added an equal volume of 48% HBr. The solution was boiled for 3-4 hours under an air condenser in such manner that the readily volatile compounds (methyl and ethyl acetate, alcohol, water, acetic acid, etc.) could vaporize until the volume of the original solution was reduced in half. Then water was passed through the condenser and the solution was boiled another 5-7 hours.* The next day the mixture was diluted with an equal volume of water and the obtained precipitate of phthalic acid (and in the synthesis of the diamino carboxylic acids also of benzoic acid) was separated, washed with 20 ml of water, and the filtrate, together with wash waters, evaporated at 10-15 mm to dryness, at the end, on the boiling water bath.** The hydrobromides of glycine, alanine and valine were dissolved in 100 ml of water, the solution treated with excess silver carbonate paste (thoroughly washed free of ions) until the test for Br' was negative, and the precipitate separated and washed with 20-30 ml of hot water. After precipitating the Ag' with hydrogen sulfide, the solution was decolorized with activated charcoal and then concentrated. The amino acid was precipitated from the nearly boiling saturated solution by the addition of 150 ml of ethanol (100 ml is sufficient for valine), the precipitate cooled for 6-8 hours at 0°, separated, washed first with 20 ml of ethanol, and then with 10 ml of ether.

Tyrosine and phenylalanine were precipitated from their hot saturated hydrobromide solutions by the addition of ammonia (using Bromocresol Purple as indicator); glutamic acid was isolated under the same conditions by the addition of a slight excess of aniline, after which the resulting suspension was treated with 60 ml of alcohol.*** After cooling for 6 hours at 0°, the amino acid precipitate was separated. Tyrosine was washed with water, while the phenylalanine and glutamic acid were triturated several times with alcohol until the filtrate gave a negative test for halide ion.

The phthaloyl derivatives of the diamino carboxylic acid esters were hydrolyzed with a mixture of 150 ml of glacial CH_3COOH, 150 ml of concentrated HCl and 150 ml of water, extending the total hydrolysis time to 22-24 hours. The solution after the removal of the phthalic and benzoic acids (see above) was evaporated, the sirupy residue was dissolved in 30 ml of alcohol, and the dihydrochloride was precipitated with 10 parts of acetone [17]; the resulting oil gradually crystallized at 0°. The ornithine and lysine monohydrochlorides were obtained as described earlier [18].

The Kjeldahl method was used to determine the total nitrogen content of the obtained labeled amino acids. The solution after titration was evaporated in vacuo to a volume of 2-3 ml, the ammonium salt was oxidized with hypobromite to nitrogen [19], and the ratio $N^{15}:N^{14}$ was determined with a mass spectrometer. The results of the analyses and mass-spectrometric measurements of the synthesized amino acids are summarized in Table 4.

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*The methyl ester of N-phthaloyl-O-methyltyrosine was hydrolyzed by dissolving it with careful heating in 250 ml of 48% HBr and then boiling for 8 hours.

**Tyrosine hydrobromide under these conditions can partially cleave HBr, forming the free amino acid; consequently, if the residue obtained after evaporation is not completely soluble in water, then 1-2 drops of HBr should be added.

***In case of need the hydrobromide solutions of phenylalanine and glutamic acid are previously decolorized with charcoal.

SUMMARY

A method was developed for the synthesis of α-N^{15}-amino acids via the condensation of potassium N^{15}-phthalimide with the esters of α-halo acids. We accomplished the synthesis of N^{15}-glycine, N^{15}-alanine, N^{15}-valine, N^{15}-glutamic acid, N^{15}-phenylalanine and N^{15}-tyrosine, and also of the monohydrochlorides of N^{15}-ornithine and N^{15}-lysine.

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REACTION OF HYDRAZINE DERIVATIVES

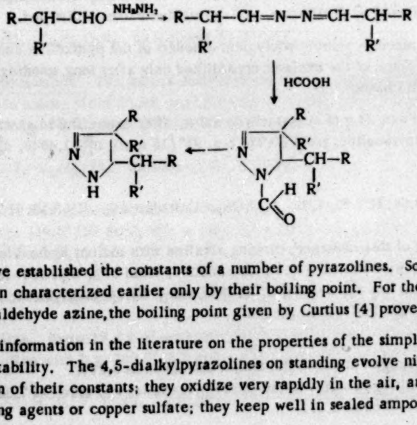
VII. CYCLIZATION OF ALDAZINES UNDER THE INFLUENCE OF ANHYDROUS FORMIC ACID

A. N. Kost and I. I. Grandberg

The azines of ketones are converted into pyrazolines under the influence of either dibasic organic acids [1] or anhydrous hydrogen halides [2]. For the aldazines this reaction is not well defined; the pyrazolines are formed only in small amounts, while the main reaction products prove to be high-boiling condensation products. Thus, from acetaldehyde azine, Curtius [3] obtained a substance with the empirical formula $C_{16}H_{26}N_6$. Propionaldehyde azine gave a condensation product of composition $C_{24}H_{42}N_6$ and only traces of a substance with b.p. 105-107° at 15 mm, assumed by Curtius to be the corresponding pyrazoline [4]. An exception is isobutyraldehyde azine, which is easily converted into 4,4-dimethyl-5-isopropylpyrazoline, even under the influence of concentrated hydrochloric acid [3].

We postulated that the NH-group of the pyrazoline participates in the condensation process, and consequently used anhydrous formic acid for the rearrangement of aldazines. This method, proposed by us earlier [5] for the rearrangement of ketazines, leads not to the pyrazolines themselves, but to their N-formyl derivatives.

Actually, with this method we were able to smoothly convert the aldazines to the corresponding N-formylpyrazolines in yields of 60-90%. Hydrolysis of the formyl derivatives gave the corresponding pyrazolines.



In this connection we established the constants of a number of pyrazolines. Some of the pyrazolines were new, while others had been characterized earlier only by their boiling point. For the pyrazoline obtained by the rearrangement of propionaldehyde azine, the boiling point given by Curtius [4] proved to be in error.

There is very little information in the literature on the properties of the simpler pyrazolines. This is possibly explained by their instability. The 4,5-dialkylpyrazolines on standing evolve nitrogen gas bubbles, which complicates determination of their constants; they oxidize very rapidly in the air, and vigorously evolve nitrogen when treated with oxidizing agents or copper sulfate; they keep well in sealed ampoules.

EXPERIMENTAL

Propionaldehyde azine. To a mixture of 116 g (2 moles) of propionaldehyde and 200 ml of ether was added, in drops, 52 g (1 mole) of 96% hydrazine hydrate. Then (in 15 minutes) 35 g of potash was added, the oil layer was separated, shaken with 20 g of anhydrous magnesium sulfate, and distilled. The yield of azine was 84.2 g (75.2%), b.p. 134-139° (736.5 mm). After a second distillation, b.p. 137° (736 mm), n_D^{20} 1.4474, d_4^{20} 0.8318, MR_D 35.73; calc. 35.98.• Literature: b.p. 143-145°, n_D^{18} 1.379 (?), d_4^{19} 0.844 [3].

Acetaldehyde azine. Obtained in a manner similar to the preceding from 22 g of acetaldehyde (0.5 mole); yield 66.7%, b.p. 85-86° (744 mm), n_D^{20} 1.4404, d_4^{20} 0.8356, MR_D 26.53; calc. 26.75. Literature: b.p. 95-97° [6], 95-96° (760 mm), d^{17} 0.832 [3].

Hexanal azine. To 86 g (0.85 mole) of hexanal was added, in drops, 22.1 g (0.425 mole) of 96% hydrazine hydrate and the mixture was allowed to stand for a day. Then 100 ml of ether was added, the organic layer was separated, dried over magnesium sulfate, the ether distilled off, and the residue vacuum-distilled. The yield of azine with b.p. 139-143° (20 mm) was 63.5 g (64.8%). After a second distillation, b.p. 139° (21 mm), n_D^{20} 1.4621, d_4^{20} 0.8500, MR_D 63.50; calc. 63.69. Literature: b.p. 242-250° [2].

Isovaleraldehyde azine. Obtained in a similar manner from 100 g of isovaleraldehyde; yield 90.5%, b.p. 92-95° (21 mm). After a second distillation, b.p. 93° (20 mm), n_D^{20} 1.4549, d_4^{20} 0.8442, MR_D 54.07; calc. 54.46. Literature: b.p. 205-210° at 764 mm [6].

Butyraldehyde azine. Obtained in a similar manner from 100 g of butyraldehyde. Yield 80%, b.p. 78-81° (26 mm). The fraction with b.p. 80° (26 mm) had n_D^{20} 1.4520, d_4^{20} 0.8315, MR_D 45.49; calc. 45.22.

Found %: N 19.16, 19.24. $C_8H_{16}N_2$. Calculated %: N 19.27.

Isobutyraldehyde azine was obtained from 200 g of the aldehyde; yield 87.2%, b.p. 87-89° (79 mm). The fraction with b.p. 88° (79 mm) had n_D^{20} 1.4472, d_4^{20} 0.8247, MR_D 45.44; calc. 45.22. Literature: b.p. 160-165° [6].

Preparation of pyrazolines. To 9.2 g (0.2 mole) of anhydrous formic acid was added in 15-20 minutes 0.1 mole of the azine, and the mixture was allowed to stand for a day. Then the mixture was made strongly alkaline with concentrated aqueous ammonia solution and extracted 3 times with 20 ml portions of ether. (In the case of acetaldehyde azine the aqueous layer was extracted with ether in an extractor for 48 hours). The ether extracts were dried over magnesium sulfate, the ether was removed by distillation, and the residue was vacuum-distilled. A mixture of the obtained N-formylpyrazoline (0.05 mole) with 25 ml of concentrated hydrochloric acid was evaporated in a porcelain dish to half volume, made strongly alkaline with concentrated aqueous ammonia solution, and extracted 3 times with 25 ml portions of ether. The ether extracts were dried over either potash or magnesium sulfate, the ether removed by distillation, and the residue vacuum-distilled.

The oxalates were obtained by mixing equivalent amounts of the pyrazoline and anhydrous oxalic acid, both dissolved in absolute ether. Some of the oxalates crystallized only after long standing. All of the salts are formed well only from freshly distilled bases.

5-Methylpyrazoline. From 84 g of acetaldehyde azine, after extraction in an extractor for 48 hours, we obtained 1-formyl-5-methylpyrazoline; yield 60.7%, b.p. 91° (15 mm), n_D^{20} 1.4949, d_4^{20} 1.0945, MR_D 29.84; calc. 30.31. ••

Found %: C 53.61, 53.64; H 7.23, 7.39. $C_5H_8ON_2$. Calculated %: C 53.55; H 7.19.

After hydrolyzing 34 g of this substance, making alkaline with sodium hydroxide, and extracting with ether (in an extractor for 48 hours), we obtained 5-methylpyrazoline; yield 80%, b.p. 151-155° (749.5 mm). The fraction with b.p. 152° (749.5 mm) had n_D^{20} 1.4788, d_4^{20} 0.9785, MR_D 24.34; calc. 24.34. Literature: b.p. 68° (45 mm) [3]. Melting point of the picrate 141° (from alcohol).

•The refraction for the two nitrogen atoms in the azines was taken as 8.277.

••The refraction for the two nitrogen atoms in the formylpyrazolines was taken as 7.034. For the pyrazolines, not substituted on nitrogen, it was taken as 5.871.

Found %: N 22.25, 22.32. $C_{10}H_{11}O_7N_5$. Calculated %: N 22.37.

4-Methyl-5-ethylpyrazoline. The 1-formyl-4-methyl-5-ethylpyrazoline was obtained from 60 g of propionaldehyde azine; yield 67.3%, b.p. 146-154° (33-35 mm). After a second distillation, b.p. 150° (35 mm), n_D^{20} 1.4876, d_4^{20} 1.0160, MR_D 39.72; calc. 39.37.

Found %: C 66.31, 66.52; H 9.49, 9.53. $C_7H_{12}ON_2$. Calculated %: C 66.63; H 9.58.

4-Methyl-5-ethylpyrazoline was obtained by the hydrolysis of 37 g of this substance; yield 39.8%, b.p. 83-85° (18 mm), n_D^{20} 1.4647, d_4^{20} 0.9271, MR_D 33.13; calc. 33.58. Literature: b.p. 105-107° at 18 mm (?) [4]. Melting point of the oxalate 104-105° (from anhydrous alcohol),

Found %: N 14.27, 14.45. $C_{14}H_{26}O_4N_4$. Calculated %: N 14.65.

4-Ethyl-5-propylpyrazoline. The formyl derivative of 4-ethyl-5-propylpyrazoline was obtained from 160 g of butyraldehyde azine; yield 64.8%, b.p. 150-151° (33 mm), n_D^{20} 1.4797, d_4^{20} 0.9788, MR_D 48.80; calc. 48.61.

Found %: C 64.17, 64.20; H 9.66, 9.69. $C_9H_{16}ON_2$. Calculated %: C 64.24; H 9.58.

Hydrolysis in the usual manner of 84 g of the formyl derivative gave the pyrazoline; yield 51.6%, b.p. 102-103° (18 mm), n_D^{20} 1.4682, d_4^{20} 0.9130, MR_D 42.71; calc. 42.81.

Found %: N 20.02, 20.08. $C_8H_{16}N_2$. Calculated %: N 19.98.

4,4-Dimethyl-5-isopropylpyrazoline. The formyl derivative of 4,4-dimethyl-5-isopropylpyrazoline was obtained from 190 g of isobutyraldehyde azine; yield 79%, b.p. 108-110° (15 mm). The fraction with 109° (15 mm) had n_D^{20} 1.4824, d_4^{20} 0.9840, MR_D 48.77; calc. 48.61.

Found %: H 16.79, 16.85. $C_9H_{16}ON_2$. Calculated %: N 16.65.

The hydrolysis of 90 g of this substance gave the pyrazoline; yield 81%, b.p. 96-99° (34 mm). The fraction with b.p. 97.5° (34mm) had n_D^{20} 1.4619, d_4^{20} 0.9013, MR_D 42.76; calc. 42.81. Melting point of the hydrochloride 148° (from alcohol). Melting point of the oxalate 109.5° (from anhydrous alcohol). Literature: b.p. 202.5°, melting point of the hydrochloride 149° [2].

Found %: N 15.15, 15.21. $C_{18}H_{34}O_4N_4$. Calculated %: N 15.12.

4-Isopropyl-5-isobutylpyrazoline. The formyl derivative of 4-isopropyl-5-isobutylpyrazoline was obtained from 110 g of isovaleraldehyde azine; yield 88.9%, b.p. 139-141° (13 mm). The fraction with b.p. 140.5° (13 mm) had n_D^{20} 1.4762, d_4^{20} 0.9536, MR_D 58.07; calc. 57.84.

Found %: N 13.96, 14.37. $C_{11}H_{20}ON_2$. Calculated %: N 14.26.

Hydrolysis of 110 g of the formyl derivative gave the pyrazoline; yield 79.8%, b.p. 118-120° (22 mm). After a second distillation, b.p. 119.5° (22 mm), n_D^{20} 1.4643, d_4^{20} 0.8960, MR_D 51.85; calc. 52.05. M.p. of the oxalate 123° (from anhydrous alcohol).

Found %: N 12.77, 12.93. $C_{24}H_{42}O_4N_4$. Calculated %: N 13.13.

4-Butyl-5-amylpyrazoline. From 19.6 g of hexanal azine we obtained 12.4 g (55.4%) of the formyl derivative of 4-butyl-5-amylpyrazoline with b.p. 159.5° (8.5 mm), n_D^{20} 1.4769, d_4^{20} 0.9445, MR_D 67.09; calc. 67.08.

Found %: C 69.79, 69.83; H 10.57, 10.69. $C_{13}H_{24}ON_2$. Calculated %: C 69.60; H 10.78.

The hydrolysis of 11.2 g of this substance gave 9.0 g (91.2%) of the pyrazoline with b.p. 160-162° (24 mm). The fraction with b.p. 160.5° (24 mm) had n_D^{20} 1.4680, d_4^{20} 0.8911, MR_D 61.24; calc. 61.29. Melting point of the oxalate 80° (from a mixture of anhydrous alcohol and absolute ether 2:1).

Found %: N 11.21, 11.48. $C_{26}H_{50}O_4N_4$. Calculated %: N 11.62.

SUMMARY

Under the influence of anhydrous formic acid the aldazines, having an α-hydrogen atom, are converted in good yields into the 1-formyl-4,5-dialkylpyrazolines, the hydrolysis of which gives the 4,5-dialkylpyrazolines themselves.

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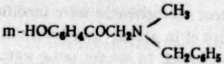
STUDY OF FATTY AROMATIC AMINO ALCOHOLS

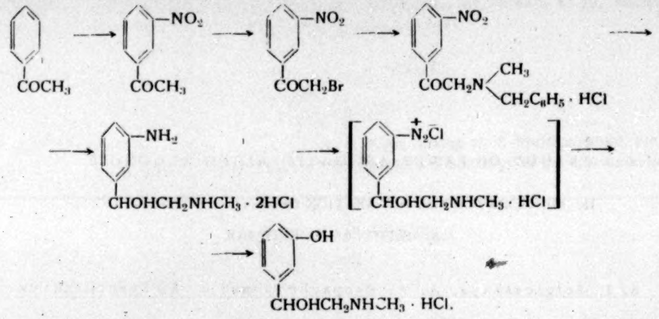
II. METHODS FOR THE PREPARATION OF α-(m-HYDROXYPHENYL)-β-METHYLAMINOETHANOL

S. I. Sergievskaya, A. A. Kropacheva and L. E. Sventsitskaya

The fairly broad method of obtaining α-aryl-β-alkylaminoethanols by the condensation of haloacetophenones with benzylalkylamines and subsequent reduction of the benzylalkylacetophenones to arylaklylaminoethanols was used by S.I. Sergievskaya and G.A. Ravdel [1] to obtain the known sympathomimetic agent – α-(m-hydroxyphenyl)-β-methylaminoethanol ($m\text{-}HOC_6H_4CH(OH)CH_2NHCH_3$). Starting with m-nitroacetophenone, m-hydroxy-ω-(methylbenzylamino)-acetophenone  $m\text{-}HOC_6H_4COCH_2N\begin{smallmatrix}CH_3\\ CH_2C_6H_5\end{smallmatrix}$ was obtained by a sequence of transformations. Hydrogenation of the latter in the presence of palladium catalyst gave the m-hydroxyphenylmethylaminoethanol.

It seemed to us that to accomplish the hydrogenation of m-hydroxy-ω-(methylbenzylamino) acetophenone on a larger scale, it would be more convenient to use a nickel catalyst. In the present study we investigated the hydrogenation of the hydrochloride of m-hydroxy-ω-(methylbenzylamino) acetophenone in the presence of skeletal nickel catalyst (A. A. Kropacheva). The hydrogenation was run under various conditions (the hydrogen pressure, temperature, solvent, etc. were varied) and it was found that the best results are obtained at a hydrogen pressure of 20-30 atm and a temperature of 50-60°. However, the m-hydroxyphenylmethylaminoethanol hydrochloride obtained after hydrogenation always contains nickel salts as impurity, which cannot be removed only by recrystallization. This difficulty is easily surmounted if the substance is purified by converting the hydrochloride to the free m-hydroxyphenylmethylaminoethanol by means of aqueous ammonia solution. In this case the m-hydroxyphenylmethylaminoethanol deposits as a crystalline precipitate and does not require further purification, while the nickel salts remain in the aqueous ammoniacal solution. Treatment of the m-hydroxyphenylaminoethanol with hydrochloric acid (1:1) again gives the hydrochloride, this time free of inorganic impurities; its yield is 70%, based on starting m-hydroxy-ω-(methylbenzylamino)-acetophenone. In the above cited paper [1] it was also indicated that α-(m-hydroxyphenyl)-β-(methylamino) ethanol can be obtained from α-(m-aminophenyl)-β-(methylamino) ethanol by the diazotization of the latter and subsequent hydrolysis of the diazo compound.

This reaction was run only for the purpose of proving the structure of the m-aminophenylmethylaminoethanol, at the time still not described in the literature. At the present time, when the m-aminophenylmethylaminoethanol is a fully available substance [2], the question arises as to the practicality of synthesizing the m-hydroxyphenylmethylaminoethanol with the same starting substance (m-nitroacetophenone) through the m-aminophenylmethylaminoethanol by the following scheme which is shorter than the one where the amino group is replaced by the hydroxy group in the initial stages of the synthesis and where the material subjected to hydrogenation is the m-hydroxy-ω-(methylbenzylamino) acetophenone:



In the present study the final stages of the presented scheme (diazotization of the m-aminophenylmethylaminoethanol, hydrolysis of the diazo compound, isolation and purification of the m-hydroxyphenylmethylaminoethanol) were investigated in two ways: in one case the m-aminophenylmethylaminoethanol, obtained by an earlier described method, was subjected to diazotization, while in the other case the conditions for the hydrogenation of the m-nitro-ω-(methylbenzylamino) acetophenone were modified (the hydrogenation was also run in the presence of palladium, but in water, instead of in alcohol solution); this last circumstance made it possible, not isolating the m-aminophenylmethylaminoethanol, to use the same water solution, after hydrogenation containing the dihydrochloride of the m-aminophenylmethylaminoethanol, for the diazotization and subsequent transformations. The methods used to isolate and purify the hydrochloride of the m-hydroxyphenylmethylaminoethanol were the same for both cases. In our opinion, the second path is the more convenient of the two for the preparation of the m-hydroxyphenylmethylaminoethanol.

EXPERIMENTAL

Preparation of the hydrochloride of α-(m-hydroxyphenyl)-β-(methylamino) ethanol from m-hydroxyphenyl-ω-(methylbenzylamino)-acetophenone. In an autoclave was placed 20 g of m-hydroxy-ω-(methylbenzylamino) acetophenone hydrochloride, 145 g of methanol and 0.3-0.4 g of skeletal nickel catalyst, the autoclave was filled with hydrogen to a pressure of 20-30 atm, and the hydrogenation run at 50-60°. On conclusion of hydrogen absorption the catalyst was filtered and the filtrate was distilled under slight vacuum to remove the methanol. The residue crystallized on standing, it was dissolved in water, and the water solution was shaken with charcoal. After removal of the charcoal, the water solution was cooled to 10-15° and to it, with stirring, was added about 10 ml of ammonia (20%); here the m-hydroxyphenylmethylaminoethanol gradually deposited as a precipitate, which was filtered and then thoroughly washed with water. The hydrochloride of the α-(m-hydroxyphenyl)-β-(methylamino) ethanol was obtained by adding hydrochloric acid (1:1) to a suspension of the hydroxyphenylmethylaminoethanol in water until slightly acid. The resulting water solution was evaporated in vacuo on the water bath at 50-60°, the residue was dissolved in a small amount of alcohol, the alcohol was vacuum-distilled to incipient crystallization of the substance, and then 6-7 ml of dry acetone was added; the obtained substance was separated and washed several times with acetone. The yield of the m-hydroxyphenylmethylaminoethanol hydrochloride with m.p. 142-145° was 9 g (about 70%).

Preparation of α-(m-hydroxyphenyl)-β-(methylamino) ethanol from α-(m-aminophenyl)-β-(methylamino) ethanol. To a cooled solution of 2.5 g of α-(m-aminophenyl)-β-(methylamino) ethanol (m.p. 84-85°) in 25 ml of 10% hydrochloric acid was added the theoretical amount of 0.5 N sodium nitrite solution at such a rate that the temperature of the reaction mass did not exceed 3-5°, after which the reaction mass was heated for 20-30 minutes at 75-78°. The end of decomposition for the diazo compound was checked by testing with an alkaline solution of β-naphthol. On conclusion of reaction, the water was vacuum-distilled, the residue dissolved in ethyl alcohol, the solution treated with sodium bicarbonate, then filtered to remove mineral salts, and the alcohol distilled in vacuo. The residual substance was dissolved in 2.5 ml of water and then ammonia gas was bubbled through the solution. The obtained precipitate of α-(m-hydroxyphenyl)-β-(methylamino) ethanol was filtered, and washed with water. The yield of substance with m.p. 146-150° was 1.9 g (76%). Recrystallization from alcohol gave 1.6 g of substance (64%) with m.p. 157-158°. The obtained substance was treated with hydrochloric acid (1:1) until weakly acid to Congo, the water was distilled off, and the residue was triturated with acetone. Here we obtained 1.92 g (51.6% yield, based on the m-nitromethylbenzylaminoacetophenone) of α-(m-hydroxyphenyl)-β-(methylamino) ethanol hydrochloride with m.p. 142-144°.

Preparation of α-(m-hydroxyphenyl)-β-(methylamino) ethanol hydrochloride from m-nitro-ω-(benzylmethylamino) acetophenone hydrochloride without isolation of the α-(m-aminophenyl)-β-(methylamino) ethanol. To a solution of 12.8 g of m-nitro-ω-(benzylmethylamino) acetophenone hydrochloride in 75 ml of water was added a solution of 1.28 g of palladium chloride in 5 ml of water and 2.3 ml of concentrated hydrochloric acid, and the whole was shaken in a hydrogen atmosphere at 30-35°. The hydrogen absorption after 4.5 hours was 4.8 liters. After removal of the catalyst, the aqueous solution was treated with 20 ml of concentrated hydrochloric acid and the diazotization run at 3-5°, using 0.5 N sodium nitrite solution; sitrring was continued for 10 minutes. The diazo compound was decomposed by rapidly heating the reaction mass to 78°, after which the water was vacuum-distilled, while the residual oil was dissolved in ethyl alcohol and the excess hydrochloric acid neutralized by the addition of sodium bicarbonate. Further treatment was exactly the same as in the preceding experiment. Recrystallization from alcohol gave the α-(m-hydroxyphenyl)-β-(methylamino) ethanol with m.p. 157-158°. The hydrochloride was obtained from the α-(m-hydroxyphenyl)-β-(methylamino) ethanol by the method described in the preceding experiment; here we obtained 4 g with m.p. 142-144°. The yield was 49%, based on starting m-nitromethylbenzylaminoacetophenone.

SUMMARY

1. The hydrogenation of m-hydroxy-ω-(methylbenzylamino)-acetophenone to α-(m-hydroxyphenyl)-β-(methylamino) ethanol in the presence of skeletal nickel catalyst was described.

2. The optimum conditions for the diazotization of α-(m-aminophenyl)-β-(methylamino) ethanol, the subsequent hydrolysis of the diazo compound, and the isolation and purification of the α-(m-hydroxyphenyl)-β-(methylamino) ethanol, formed as a result of the indicated reactions, were outlined.

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*T.p. = C. B. Translation pagination.

was filtered, and washed with water. The yield of substance with m.p. [illegible] was [illegible]. Recrystallization from alcohol gave 1.4 g of substance [illegible] with m.p. [illegible]. The [illegible] (1:1) [illegible] with acetone. Here we obtained [illegible] g [illegible] yield [illegible] α-(m-hydroxyphenyl)-β-[illegible] m.p. [illegible]°C.

Preparation of α-(m-hydroxyphenyl)-[illegible] (under investigation) a [illegible]. To a solution of 12.2 g of [illegible] was added a solution of 1.28 g of palladium chloride in [illegible] and the whole was shaken in a hydrogen atmosphere [illegible]. After removal of the catalyst, the aqueous solution [illegible] and the diazotization run at 0-5°, using [illegible] sodium nitrite [illegible]. The diazo compound was decomposed by rapidly heating the [illegible] distilled, when the residual oil was dissolved in ether [illegible] solution of sodium bicarbonate. Further treatment [illegible] as in the preceding [illegible] crystallization from alcohol gave the α-(m-hydroxyphenyl)-[illegible] obtained [illegible] m.p. [illegible] or [illegible].

SUMMARY

The hydrogenation of [illegible] alcohol in the presence of [illegible] further substances.

[illegible]

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*See C. B. Translation pagination.

SYNTHESIS OF THREONINE PEPTIDES. I

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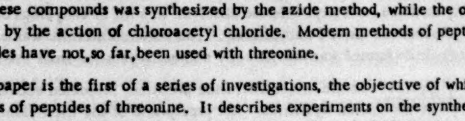
Researches carried out over the last decade have demonstrated the special position of β-hydroxy-α-aminoacids as structural elements of the protein molecule and in nitrogen exchange. They take part in the metabolism of a number of aminoacids – cystine, methionine, tryptophane and glycine [1]. In the protein molecule they determine the labile character of the peptide linkage and the migration of the peptide radical during hydrolysis [2]. The hydroxyl groups of serine become points of attack by a number of ferments [3]. Phosphoric acid combines with the protein portion of phosphoroproteins via the hydroxyl groups of serine and threonine [4]. All these facts point to the necessity for a detailed investigation of the specific properties of β-hydroxy-α-aminoacids and of their peptides.

In a series of previous communications we have described our investigations on peptides of serine. We demonstrated the ability of the peptide radical in serine peptides to migrate [5]; we determined the conditions for the synthesis of N-benzoyl-O-peptides of serine [6] and we established the possibility of hydrolysis of the O-peptidic (ether) linkage by ferments [7].

The peptides of threonine have been investigated very little. So far only three peptides of threonine have been described, namely the methyl ether of N-tosylthreonylthreonine [8], glycylthreonine and diglycylthreonine [9]. The first of these compounds was synthesized by the azide method, while the other two were obtained by Fischer's method – by the action of chloroacetyl chloride. Modern methods of peptide synthesis by means of the mixed anhydrides have not, so far, been used with threonine.

The present paper is the first of a series of investigations, the objective of which is to examine the specific characteristics of peptides of threonine. It describes experiments on the synthesis of these peptides, using mixed anhydrides (according to Vaughan and Osato [10]). The anhydride used – that of carbobenzoxyaminoacid and isovaleric acid – was reacted with the ester of the aminoacid. In order to avoid unnecessary operations (esterification of threonine and hydrolysis of its peptide) and their attendant losses, the experiments described here were carried out directly, using threonine. The possibility of carrying out such a reaction was confirmed by a preliminary synthesis of carbobenzoxyglycylglycine, which was obtained in a yield of 52%. All the subsequent experiments were carried out, using allothreonine, obtained by the method of Carter and Zirkle [11].

The mixed anhydride was obtained by the reaction of equimolecular amounts of isovaleryl chloride and the triethylamine salt of the carbobenzoxyaminoacid, dissolved in dioxan, at a temperature of about 8° C. To the mixed anhydride obtained was added an aqueous solution of the (sodium) salt of allothreonine. Upon acidification, the carbobenzoxy peptide precipitated.



$$C_4H_9COCl + C_6H_5CH_2OCONHCH(R)COOH \cdot (C_2H_5)_3N \longrightarrow$$

$$\longrightarrow C_4H_9COOCOCH(R)NHOCOCH_2C_6H_5 + (C_2H_5)_3N \cdot HCl$$

$$C_4H_9COOCOCH(R)NHOCOCH_2C_6H_5 + CH_3CHOH\underset{\displaystyle NH_2}{\underset{|}{CH}}COONa \longrightarrow$$

$$\longrightarrow C_6H_5CH_2OCONHCH(R)CONH\underset{\displaystyle CHOHCH_3}{\underset{|}{CH}}COONa.$$

The following were prepared: carbobenzoxyphenylalanyl-allothreonine, carbobenzoxylalanyl-allothreonine and carbobenzoxynorleucyl-allothreonine. After hydrogenation over palladium black, the corresponding peptides of allothreonine were obtained. The results of the experiments are given in the table.

Carbobenzoxy derivatives of allothreonine peptides	Yield, %	Melting Point	Allothreonine peptides	Yield, %
Carbobenzoxyphenylalanyl-allothreonine	29	133-135°	Phenylalanyl-allothreonine	85
Carbobenzoxyalanyl allothreonine	20.5	160	Alanyl-allothreonine	87
Carbobenzoxynorleucyl-allothreonine	19.5	120-121	Norleucyl-allothreonine	84

As will be seen from the results obtained, the yield of carbobenzoxy derivatives of threonine peptides did not exceed 30%. The difficulty and slowness of acylation of the amino group of β-hydroxy-α-aminoacids have frequently been mentioned in the literature. These difficulties, of course, have been encountered in experiments with mixed anhydrides, which always underwent hydrolysis to a considerable extent. This is shown by the fact that, together with the carbobenzoxy derivatives of the peptides, derivatives of the carbobenzoxyaminoacid were also formed: 38.8% of carbobenzoxyphenylalanine and 65% of carbobenzoxynorleucine. Substitution of the carbobenzoxy group with hydrogen over palladium black proceeded smoothly, and the peptides were obtained in high yields.

EXPERIMENTAL

I. Synthesis of Carbobenzoxy Derivatives of Glycine and Allothreonine Peptides

1. Mixed anhydride of carbobenzoxyglycine and isovaleric acid. A solution of 1.6 g carbobenzoxyglycine and 0.76 g of triethylamine in 12 ml of anhydrous dioxan was cooled to about 8°, and to it was added, with shaking, 0.9 g of freshly distilled isovaleryl chloride dissolved in 3 ml of anhydrous dioxan. A white precipitate of triethylamine hydrochloride formed immediately. The reaction mixture was cooled for 30 minutes with stirring. The mixed anhydride formed was used directly without separation from the reaction mixture.

2. Carbobenzoxyglycylglycine. To the mixed anhydride prepared, indicated above, was added a solution of 0.57 g of glycine in 1.9 ml of 4 N sodium hydroxide. The precipitate of the triethylamine salt passed into solution. After acidification with 3 N hydrochloric acid (Congo red), an oil separated. The reaction mixture was extracted with 50 ml of ether. Within a few minutes, a flaky precipitate of carbobenzoxyglycylglycine began to separate from the ether extract. The filtrate was evaporated, a further quantity of the substance being obtained. The carbobenzoxyglycylalanine was recrystallized from aqueous methyl alcohol. Yield 1.05 g (52%), m.p. 176-177° (literature, m.p. 176-177°).

3. Carbobenzoxyphenylalanyl-allothreonine. To the mixed anhydride, prepared from 1.68 g carbobenzoxyphenylalanine and isovaleric acid, as described above, was added 0.67 g threonine dissolved in 1.4 ml of 4 N alkali. The solution was stirred, acidified with 4 N hydrochloric acid and diluted with water (25 ml) until separation of the oil ceased. The oil was extracted with ether. After removal of the ether and treatment of the residual oil with benzene crystals of unreacted carbobenzoxyphenylalanine, 0.65 g (33.8%), m.p. 102°, separated.

The water-dioxan solution was concentrated under vacuum and extracted with 50 ml ether. The ether extracts were concentrated under vacuum and the residual oil evaporated several times under vacuum with anhydrous benzene. During the process crystallization occurred. The crystals were separated and washed with ether. Yield of carbobenzoxyphenylalanyl-allothreonine was 0.68 g (30%), m.p. 133-135°. The substance is soluble in dioxan and alcohol, sparingly soluble in chloroform, carbon tetrachloride, ether, and benzene, and insoluble in water.

Found %: C 62.60, 62.62; H 6.11, 6.03; N 7.29, 7.10. $C_{21}H_{24}O_6N_2$. Calculated %: C 63.0; H 6.0; N 7.0.

4. Carbobenzoxynorleucyl-allothreonine. To the mixed anhydride obtained from 1 g carbobenzoxynorleucine was added a solution of 0.45 g allothreonine in 0.96 ml of 4 N alkali. The reaction mixture was

stirred, acidified with 4 N hydrochloric acid and diluted with 30 ml water until separation of the oil ceased. The latter crystallized on standing during the day. The crystals were recrystallized from aqueous alcohol. M.p. 105°. The mixed sample with carbobenzoxynorleucine did not give a depression of the melting point. Yield 0.65 g.

The filtrate obtained after separating the crystals was evaporated under vacuum to 5 ml and extracted with ether. The ether solution was evaporated under vacuum and the residual oil, after washing with ether, crystallized after repeated treatment with anhydrous benzene. Yield 0.27 g (19.5%), m.p. 120-121°. Carbobenzoxynorleucyl-allothreonine is soluble in alcohol and dioxan, sparingly soluble in ether, carbon tetrachloride, and chloroform, and insoluble in water.

Found %: C 59.30, 59.43; H 7.29, 7.21; N 7.95, 7.89. $C_{18}H_{26}O_6N_2$. Calculated %: C 59.01; H 7.10; N 7.65.

5. Carbobenzoxyalanyl-allothreonine. To the mixed anhydride obtained from 0.85 g of carbobenzoxyalanine, was added 0.45 g of allothreonine, dissolved in 0.96 ml of 4 N alkali. The solution was stirred, acidified with 4 N hydrochloric acid, diluted with 50 ml of water until separation of the oil ceased, and was then extracted with ether. After evaporation of the ether extract under vacuum, a residual oil was obtained which crystallized after treatment with anhydrous benzene. M.p. 113°. The melting point of a mixture with carbobenzoxyalanine was not depressed. The yield of unreacted carbobenzoxyalanine was 0.38 g.

The aqueous dioxan mother liquor left after the ether extraction was evaporated in vacuum to 15 ml and extracted with ether. The ether extracts were evaporated in vacuum. The residue, a colorless oil, was repeatedly evaporated in vacuum with anhydrous benzene and crystallized partially. The crystals were separated and washed with ether. The melting point of the carbobenzoxyalanyl-allothreonine, 160°, was unchanged after recrystallization from aqueous alcohol. Yield 0.25 g (20.3%). The substance is soluble in alcohol and dioxan, sparingly soluble in benzene, ether, carbon tetrachloride and chloroform, and insoluble in water.

Found %: C 55.18, 55.24; H 6.52, 6.35. $C_{15}H_{20}O_6N_2$. Calculated %: C 55.55; H 6.17.

II. Preparation of Peptides of Allothreonine

To the solution of carbobenzoxy peptide (0.15 g in 20 ml of alcohol) was added 1 ml of water, 1 ml glacial acetic acid and 0.02 g palladium black. A current of hydrogen was passed through the solution at room temperature. At the end of the hydrogenation, water was added to the cloudy solution until the precipitate redissolved, the catalyst was filtered, and the solution was evaporated in vacuum. The residue consisted of a colorless or yellow oil which crystallized after treatment with aqueous alcohol. In this manner, the following compounds were obtained:

Norleucyl-allothreonine in 0.08 g (84%) yield.

Found %: C49.61, 49.62; H 9.09, 9.08. $C_{10}H_{20}O_4N_2 \cdot \frac{1}{2}\ H_2O$. Calculated %: C 49.77; H 8.71.

Alanyl-allothreonine in 0.054 g (87%) yield.

Found %: C 44.62, 44.56; H 7.44, 7.56. $C_7H_{14}O_4N_2$. Calculated %: C 44.21; H 7.37.

Phenylalanyl-allothreonine in 0.085 g (85%) yield.

Found %: C 58.48, 58.42; H 7.08, 7.05. $C_{13}H_{18}O_4N_2$. Calculated %: C 58.64; H 6.99.

SUMMARY

The authors have demonstrated the possibility of using the method of mixed anhydrides in the synthesis of peptides of threonine. The following compounds have been synthesized: phenylalanyl-allothreonine, alanyl-allothreonine, and norleucyl-allothreonine and their carbobenzoxy derivatives.

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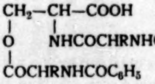
* T.p. = C. B. Translation pagination.

SYNTHESIS OF N-BENZOYL-O-PEPTIDES OF THREONINE AND ALLOTHREONINE AND OF THEIR METHYLAMIDES. II.

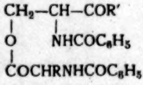
S. M. Avaeva and M. M. Botvinik

In our previous papers we have resolved the problem of the possibility of the formation of the O-peptidic linkage through the hydroxyl group of serine, and we have established the conditions of synthesis of a number of N, O-peptides of serine (A), N-benzoyl-O-peptides of serine and their derivatives (B) [1], and we have synthesized such compounds.



$$\begin{array}{l} CH_2{-}CH{-}COOH \\ |\qquad\; | \\ O \quad NHCOCHRNHCOC_6H_5 \\ | \\ COCHRNHCOC_6H_5 \end{array}$$

(A)

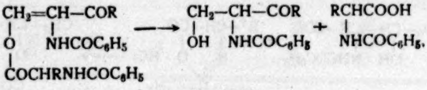


$$\begin{array}{l} CH_2{-}CH{-}COR' \\ |\qquad\; | \\ O \quad NHCOC_6H_5 \\ | \\ COCHRNHCOC_6H_5, \end{array}$$

(B)

where $R' = OH, NHCH_3, OC_2H_5$.

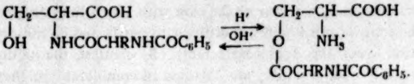
The stability of the O-peptide linkage in acid and alkaline media has been investigated and it has been shown for the first time that the O-peptide linkage can be ruptured by the action of ferments [2].



$$\begin{array}{l} CH_2{=}CH{-}COR \\ |\qquad\; | \\ O \quad NHCOC_6H_5 \\ | \\ COCHRNHCOC_6H_5 \end{array} \longrightarrow \begin{array}{l} CH_2{-}CH{-}COR \\ |\qquad\; | \\ OH \quad NHCOC_6H_5 \end{array} + \begin{array}{l} RCHCOOH \\ | \\ NHCOC_6H_5, \end{array}$$

where $R = OH, NHCH_3$

We have also shown that, under the action of acidic agents, N-peptides of serine can undergo rearrangement into O-peptides of serine, the reverse reaction, promoted by alkaline agents, leading to the formation of the original N-peptide [3].



$$\begin{array}{l} CH_2{-}CH{-}COOH \\ |\qquad\; | \\ OH \quad NHCOCHRNHCOC_6H_5 \end{array} \underset{OH'}{\overset{H'}{\rightleftarrows}} \begin{array}{l} CH_2{-}CH{-}COOH \\ |\qquad\; | \\ O \quad NH_3^{\cdot} \\ | \\ COCHRNHCOC_6H_5. \end{array}$$

All the investigations have been carried out with the first member of β-hydroxyamino acids – serine. The literature records very little data on the chemical properties of peptides of the next member of hydroxyaminoacids – threonine [4].*

The present paper describes the synthesis of N-acyl-O-peptides of threonine and allothreonine. On the basis of these compounds, we shall deal in our next papers with the possibility of hydrolysis of the O-peptidic linkage in threonine peptides by fermentation. The β-hydroxy-α-amino butyric acid necessary for the synthesis of the peptides was obtained from crotonic acid by the method of Carter and Zirkle [5]. The reaction yields allothreonine, which is then changed into threonine by the Walden inversion [6].

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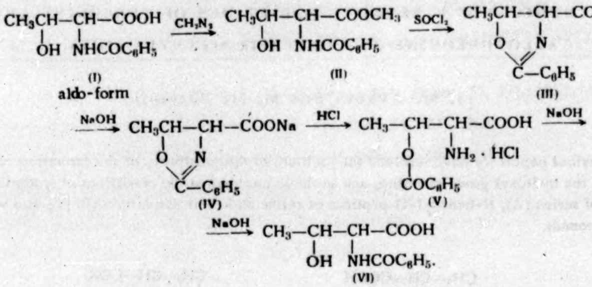
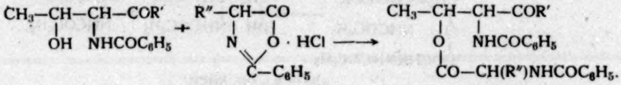
* While this paper was being made ready for press, the paper [7] on the synthesis of O-peptides of serine and threonine appeared.

The methyl ester of N-benzoylallothreonine (II) was obtained by reacting N-benzoylallothreonine (I) with diazomethane.



The methyl ester of oxazolinecarboxylic acid (III) was obtained by the action of thionyl chloride, without isolating the intermediate compounds. This was then hydrolyzed with alkali to give oxazolinecarboxylic acid (IV), which upon treatment with hydrochloric acid was converted into the hydrochloride of O-benzoyl-d,l-threonine (V). Under the action of alkali O-benzoyl-N-threonine was converted to N-benzoyl-d,l -threonine (VI).

Syntheses of N-benzoyl-O-peptides of threonine were carried out with both d,l- and allothreonines. The peptides were obtained by the same method as that used in the synthesis of similar peptides of serine. N-Benzoylthreonine or its methylamide was treated with oxazolone hydrochloride in anhydrous medium.

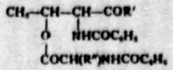


The N-benzoyl-O-peptides of threonine prepared are listed in the table. A striking feature, evident from the table, is the comparatively low yields of the peptides. This problem requires some further investigation. Although the present work was not directed toward determination of the best conditions for the synthesis, it has been possible, nevertheless, to draw certain preliminary conclusions, among them being the fact that the yield of peptides varies very little with changes in the experimental conditions. Evidently, the yield depends not only on the length of the reaction period, but also on the ease with which the compound crystallizes. The peptides (II-V) are obtained in the form of oils which are difficult to purify and do not crystallize easily. On the other hand, repeated purification lowers the yield considerably. By contrast, the methylamides of peptides (V-X) crystallize much more readily and, as a rule, are obtained in considerably higher yields than the corresponding peptides.

EXPERIMENTAL

I. Conversion of Allothreonine into N-Benzoyl-d,l-threonine

N-Benzoyl-d,l -threonine. 5 g of the methyl ester of N-benzoyl-allothreonine (m.p. 110°) was added in small portions to 12 ml of thionyl chloride, cooled to 0°. The compound dissolved with the evolution of a small quantity of gas. The solution was warmed on a water bath until the vigorous evolution of gas ceased, and was then allowed to stand for two hours at room temperature. On addition of absolute ether, a thick white precipitate of the hydrochloride of the methyl ester of 2-methyl-5-phenyloxazoline-3-carboxylate was obtained. This was

No.	Peptide	 $CH_3-CH(OCOCH(R'')NHCOC_6H_5)-CH(NHCOC_6H_5)-COR'$		Experimental conditions	Yield (%)	M. p.
		R'	R"			
I	N-Benzoyl-O-benzoylphenylalanyl-allothreonine	OH	$C_6H_5CH_2$	5.5 hours at 55-56° and one night at room temp.	24	170—170.5°
II	N-Benzoyl-O-benzoylnorleucyl-d,l-threonine	OH	$CH_3(CH_2)_3$	One night at room temp. and 4 hours at 45-50°.	47	190—191.5
III	N-Benzoyl-O-benzoylnorleucyl-allothreonine			1 hour 15 minutes at room temp. 4 hours at 45-50°	15	131—133
IV	N-Benzoyl-O-benzoylvalyl-d,l-threonine	OH	$(CH_3)_2CH$	2 days at room temp.	23	173—173.5
V	N-Benzoyl-O-benzoylphenylalanyl-d,l-threonine methylamide	$NHCH_3$	$C_6H_5CH_2$	7½ hours at 60-65° and one night at room temp.	39	219—221
VI	N-Benzoyl-O-benzoylphenyl-alanyl-allothreonine methylamide			Ditto	51	214—214.5
VII	N-Benzoyl-O-benzoylnorleucyl-d,l-threonine methylamide	$NHCH_3$	$CH_3(CH_2)_3$	8 hours at 55-60° and one night at room temp.	49	222.5—223.5
VIII	N-Benzoyl-O-benzoylnorleucyl-allothreonine methylamide			Ditto	20	205—206
IX	N-Benzoyl-O-benzoylvalyl-d,l-threonine methylamide	$NHCH_3$	$(CH_3)_2CH$	1 hour at 65-70° and one night at room temp.	40	215—216
X	N-Benzoyl-O-benzoylvalyl-allothreonine methylamide			Ditto	35	226.5—227.5

separated by decantation, washed several times with ether, and hydrolized with 80 ml of 0.5 N alkali for one hour at room temperature. It was then heated until the compound dissolved completely. The reaction mixture was cooled and acidified with 8 ml of 5 N hydrochloric acid. After 3 hours, 5 N alkali was added until a distinct alkaline reaction to phenolphthalein was obtained. On acidifying, the hot solution N-benzoyl-d,l-threonine began to crystallize in the form of very long, snow-white needles. The substance weighed 2.6 g, m.p. 144-146°; literature, m.p. 143-145° [6]. A further quantity of 0.88 g was separated from the mother liquor. Yield 3.48 g (74%).

II. Preparation of N-Benzoyl-O-peptides of Threonine

N-Benzoyl-O-benzoylphenylalanyl-allothreonine. The hydrochloride of benzoylphenylalanine, obtained from 1.7 g of benzoylphenylalanine and 1.24 g of phosphorus pentachloride in carbon tetrachloride, was suspended in anhydrous dioxan and added to a solution of 0.9 g of N-benzoyl-allothreonine in anhydrous dioxan. The precipitate of the hydrochloride soon dissolved (30 minutes). The almost clear solution was warmed for 5 $^1/_2$ hours at 55-56°, left overnight, and evaporated to dryness in vacuum. In order to isolate the peptides from the unreacted oxazolone, the residual oil was dissolved in ethyl acetate and precipitated with petroleum ether. Crystallization took place as the oil was dissolving in ethyl acetate, with the addition of small quantities of petroleum ether. The precipitated crystals were filtered and washed with benzene and repeatedly with hot water. After washing with water and recrystallization, the reprecipitated oil weighed 0.8 g. The substance was recrystallized once more from ethyl acetate to which a small quantity of petroleum ether was added. The precipitated crystals were decolorized by boiling with animal charcoal in alcoholic solution. The N-benzoyl-O-benzoylphenylalanyl-allothreonine weighed 0.35 g, m.p. 170-170.5°. Yield 24%.

Found %: C 67.11, 66.98; H 5.69, 5.68; N 5.87, 5.95. $C_{27}H_{26}O_6N_2 \cdot {}^1/_2\, H_2O$. Calculated %: C 67.08; H 5.59; N 5.79.

N-Benzoyl-O-benzoylnorleucyl-d,l-threonine. To 1.8 g of dried and sifted benzoylnorleucine was added 1.56 g of ground phosphorus pentachloride and 20 ml of anhydrous carbon tetrachloride. A reaction began at once, a considerable proportion of the material going into solution, and a thick white precipitate of benzoylnorleucine azlactone hydrochloride beginning to separate from the yellow solution. The reaction was accompanied by the evolution of heat, and was complete within 10-12 minutes. The solution was stirred for 30 minutes, filtered, and the residue suspended in 20 ml of anhydrous dioxan, and added to a solution of 0.9 g of benzoyl-d,l-threonine in 20 ml of dioxan. After one hour, the reaction mixture was almost clear. The next day, the mixture was warmed for 4 hours at 45-50°, then it was left overnight, and subsequently evaporated in vacuum. The oil obtained was dissolved in ethyl acetate and treated with a small quantity of petroleum ether. On standing, the reaction mixture solidified to a dense mass of white crystals. These were washed with ethyl acetate, benzene and hot water. Weight 1.23 g, m.p. about 180°. The N-benzoyl-O-benzoylnorleucyl-d,l-threonine was recrystallized several times from aqueous alcohol and dried at 113° (20 mm). M.p. 191-191.5°, yield 0.83 g (47%).

Found %: C 65.13, 65.03; H 6.69, 6.74; N 6.68, 6.88; equiv. wt. 447, 435. $C_{24}H_{28}O_6N_2$. Calculated %: C 65.45; H 6.36; N 6.36; equiv. wt. 440.

N-Benzoyl-O-benzoylnorleucyl-allothreonine. A solution of 0.67 g of benzoyl-allothreonine in dioxan was mixed with a suspension of benzoylnorleucine azlactone hydrochloride in dioxan (prepared from 1.4 g of benzoylnorleucine and 1.17 g of phosphorus pentachloride). The material dissolved rapidly. The reaction mixture was stirred for 1$^1/_4$ hours and warmed for 4 hours at 45-50°. The oil left after evaporation in vacuum was precipitated several times from its solution in ethyl acetate with petroleum ether, and subsequently from alcoholic solution with water. The dried and crystallized oil, weighing 0.45 g, was recrystallized from ethyl acetate with a small quantity of petroleum ether. The oily precipitate was separated by decantation and, on standing in a vacuum desiccator, solidified to a hard mass (0.3 g). This was recrystallized twice from a mixture of ethyl acetate with a small quantity of petroleum ether. Yield of N-benzoyl-O-benzoylnorleucyl-allothreonine 0.2 g (15.1%), m.p. 131-133°.

Found %: C 65.35, 65.21; H 6.65, 6.60; N 6.57, 6.58. $C_{24}H_{28}O_6N_2$. Calculated %: C 65.45; H 6.36; N 6.36.

N Benzoyl-O-benzoylvalyl-d,l -threonine. To 1.35 g of dried and sifted benzoylvaline, there was added 1.2 g of phosphorus pentachloride. A reaction started immediately, accompanied by the evolution of hydrogen chloride with the formation of a bright yellowish-green liquid. To the reaction mixture was added carbon tetrachloride. Within 3-5 minutes a voluminous white precipitate of benzoylvaline azlactone hydrochloride began to form. After 10-15 minutes the reaction subsided and the evolution of hydrogen chloride ceased. The reaction mixture was stirred for a further 30 minutes, after which the precipitate was filtered and added to a solution of 0.5 g of benzoyl-d,l -threonine in anhydrous dioxan. The benzoylvaline azlactone hydrochloride went into solution. After two days the reaction mixture was evaporated, and the residual oil was precipitated twice from its solution in ethyl acetate with petroleum ether and was subsequently digested several times with boiling water. The dried and almost solid oil was recrystallized from ethyl acetate with a small amount of petroleum ether. The isolated 0.4 g (23%) of N-benzoyl-O-benzoylvalylserine had m.p. 173-173.5°.

Found %: C 64.46, 64.38; H 6.33, 6.16; N 6.67, 6.65. $C_{23}H_{26}O_6N_2$. Calculated %: C 64.78; H 6.10; N 6.57.

III. Preparation of Methylamides of N-Benzoyl-O-peptides of Threonine

N-Benzoyl-d,l -threonine methylamide. A current of diazomethane was passed through a suspension of 4 g of benzoyl-d,l -threonine in absolute ether until the mixture assumed a constant yellowish-green coloration. The ether solution was evaporated and the residual, colorless and very thick oil (4.28 g) was treated with 30% methanol solution of methylamine. After three days, the solution was evaporated to dryness, and the N-benzoyl-d,l -threonine methylamide was recrystallized from ethyl acetate, m.p. 170-171°. Yield 2.73 g (64%).

Found %: C 61.02, 61.19; H 6.97, 6.92; N 11.76, 11.57. $C_{12}H_{16}O_3N_2$. Calculated %: C 61.01; H 6.78; N 11.78.

N-Benzoyl-allothreonine methylamide was prepared by a method similar to that used for the preparation of the methylamide of N benzoyl-d, l-threonine. Yield 51%; m.p. 180-182°.

Found %: C 61.44, 61.47; H 7.13, 7.08; N 11.84, 12.03. $C_{12}H_{16}O_3N_2$. Calculated %: C 61.01; H 6.78; N 11.78.

N-Benzoyl-O-(benzoylphenylalanyl)-d,l -threonine methylamide. To a solution of 0.95 g of benzoyl-d,l -threonine methylamide in dioxan was added a solution of benzoylphenylalanine hydrochloride in chloroform (obtained by reacting 1.6 g of benzoylphenylalanine with 1.17 g of phosphorus pentachloride). The solution was warmed for 7 1/2 hours at 60-65°, and left overnight. The precipitated residue was washed with benzene, water, sodium carbonate and again with water, and weighed 0.9 g; m.p. 199°. The substance was recrystallized from a mixture of absolute alcohol with a small amount of ethyl acetate, m.p. 219-221°. Yield 0.75 g (39%).

Found %: C 68.77, 68.77; H 6.01, 6.10; N 8.76, 8.42. $C_{28}H_{29}O_5N_3$. Calculated %: C 68.99; H 5.95; N 8.62.

N-Benzoyl-O-benzoylphenylalanyl-allothreonine methylamide was obtained from 0.47 g of benzoyl-allothreonine methylamide under conditions similar to those used in the preparation of the d,l -isomeride. After four hours of heating, voluminous precipitate (0.96 g) began to form which was filtered and washed with benzene. On recrystallization from absolute alcohol the substance was obtained in the form of thin needles, m.p. 214-214.5°, yield 0.5 g (51%).

Found %: C 69.20, 69.38; H 6.20, 6.24; N 8.60, 8.95. $C_{28}H_{29}O_5N_3$. Calculated %: C 68.99; H 5.95; N 8.62.

N-Benzoyl-O-benzoylnorleucyl-d,l -threonine methylamide. To 0.94 g of N-benzoyl-d,l -threonine methylamide in anhydrous dioxan, there was added benzoylnorleucine azlactone hydrochloride (prepared from 1.4 g of benzoylnorleucine and 1.17 g of phosphorus pentachloride) in 30 ml of chloroform, and the solution was warmed for 8 hours at 55-60°. Within 1 hour a white needle-like precipitate began to form. This was filtered the next day and washed with benzene, sodium carbonate and water, and was then recrystallized from glacial acetic acid. Yield 0.88 g (49%), m.p. 222.5-223.5°.

Found %: C 66.09, 66.02; H 7.07, 7.02; N 9.26, 9.30. $C_{25}H_{31}O_5N_3$. Calculated %: C 66.23; H 6.84; N 9.26.

N-Benzoyl-O-benzoylnorleucyl-allothreonine methylamide was obtained from 0.47 g of N-benzoyl-allothreonine methylamide under conditions similar to those used for the d,l-isomeride. However, on allowing the reaction mixture to stand, only a small quantity of the substance was precipitated, in the form of a jelly-like mass; this was separated and recrystallized by dissolving in acetic acid and precipitating with a very small quantity of water. M.p. 205-206°. Yield 0.17 g (20%). No further quantities of the compound could be isolated from the mother liquor.

Found %: C 66.00, 65.80; H 6.99, 7.07; N 9.24. $C_{25}H_{31}O_5N_3$. Calculated %: C 66.23; H 6.84; N 9.26.

N-Benzoyl-O-benzoylvalyl-d,l-threonine methylamide. To 0.8 g of benzoyl-d,l-threonine methylamide in anhydrous dioxan, was added a solution of benzoylvaline azlactone hydrochloride (prepared from 1.3 g of benzoylvaline and 1.17 g of phosphorus pentachloride), in 90 ml of chloroform, and the reaction mixture was heated for 1 hour at 65-70° and left to stand overnight at room temperature. The precipitate (0.85 g, m.p. 209-211°) was recrystallized from aqueous alcohol, m.p. 215-216°. Yield 0.59 g (40%).

Found %: C 65.64, 65.78; H 6.93, 6.76; N 9.48, 9.37. $C_{24}H_{29}O_5N_3$. Calculated %: C 65.60; H 6.61; N 9.57.

N-Benzoyl-O-benzoylvalyl-allothreonine methylamide was obtained from 0.5 g of benzoyl-allothreonine methylamide under conditions similar to those under which the d,l-isomeride was prepared. On standing, a portion of the reaction mixture jelled. To reduce the solubility of the substance, petroleum ether was added, and the reaction mixture was filtered carefully. The dried substance (0.5 g, m.p. 224-226°) was recrystallized from acetic acid, m.p. 226.5-227.5°. Yield 0.32 g (35%).

Found %: C 65.83, 65.85; H 6.81, 6.83; N 9.51, 9.71. $C_{24}H_{29}O_5N_3$. Calculated %: C 65.60; H 6.61; N 9.57.

SUMMARY

A description is given of the preparation of N-benzoyl-O-peptides of threonine and of their amides. The following compounds have been synthesized: N-benzoyl-O-benzoylphenylalanyl-allothreonine, N-benzoyl-O-benzoylnorleucyl-d,l-threonine, N-benzoyl-O-benzoylnorleucyl-allothreonine, N-benzoyl-O-benzoylvalyl-d,l-threonine, N-benzoyl-O-benzoylvalyl-allothreonine, and their methylamides.

It has been shown that the experimental conditions established previously for the preparation of N-acyl-O-peptides of serine are general for the preparation of N-acyl-O-peptides of β-hydroxy-α-aminoacids.

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SPECTROSCOPIC INVESTIGATION OF FACTORS CONDITIONING β-ELIMINATION REACTIONS OF β-HALOALKYLSILANES

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I. Experimental work of the last few years, in particular the researches of the school of Whitmore [1], have shown that among compounds which undergo with particular ease reactions leading to the formation of ethylene and other olefins (also called β-elimination reactions), belong β-halogen-substituted alkylsilanes of the type $X_3Si-CH_2CH_2-Cl$, where X may be an alkyl radical or a halogen. With some of these compounds (especially when X is an alkyl) β-elimination takes place on mere heating:

$$X_3Si-CH_2CH_2-Cl \rightarrow CH_2=CH_2 + X_3SiCl.$$

A correlation of these facts with other experimental data relating to β-haloaklylsilanes shows that the less electronegative the atom X (relative to hydrogen) and the more electronegative the atom Y, the more easily the reaction takes place with the evolution of ethylene (ethylenic hydrocarbons):

$$X-CH_2-CH_2-Y \rightarrow CH_2=CH_2 + XY.$$

β-Elimination reactions in β-haloalkylsilanes are often brought about, not only by the application of heat, but also by the action of nucleophilic (alkalis, compounds containing the alkoxy group, etc.), as well as electrophilic reagents ($AlCl_3$, etc.). It must be stressed here that if, in the compounds $X_3Si-CH_2CH_2-Cl$, the atom or group X is strongly electronegative (Cl, F, etc.), the corresponding compounds are markedly less susceptible to the β-elimination reaction. Thus, in the case of $Cl_3Si-CH_2CH_2-Cl$, simple heating no longer leads to β-elimination; this takes place only when the compound is acted upon by nucleophilic or electrophilic reagents. At the same time, the compound $Cl_3Si-CH_2CH_2-Cl$ undergoes dehydrochlorination relatively easily:

$$Cl_3Si-CH_2CH_2-Cl \xrightarrow[\text{quinoline}]{AlCl_3} Cl_3Si-CH=CH_2 + HCl.$$

When making a comparison of the β-elimination reaction and of dehydrochlorination of β-halogen-substituted alkylsilanes which interest us here, it is, therefore, necessary to stress that the compounds in question exhibit a tendency toward β-elimination or toward dehydrochlorination, depending on the structure of the given compound and on the experimental conditions, or, in varying degrees, toward both of these reactions.

We may also note that, whereas the C−X (X = Cl, Br, etc.) linkage in the β-haloalkylsilanes is very reactive in the β-position, the same linkage exhibits enhanced chemical stability in the α-position in α-haloalkylsilanes, as compared with either β-haloalkylsilanes or with the corresponding alkyl halides.

In the light of the above evidence and on the basis of results of a spectroscopic investigation of a series of organosilicon compounds, we shall attempt to elucidate the fundamental factors which influence the β-elimination reaction in β-haloalkylsilanes. Below we list the Raman spectra of some organosilicon compounds* which have been obtained by us on a triple-prism spectrograph ISP-51, with a central cell for the exciting mercury line 4358 A.*

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* Among the Raman spectra used in the present paper are also those of other organosilicon compounds, some of which have been taken from the paper [2] and from other works.

Before the spectra were recorded, the compounds were distilled twice on a column of 35 theoretical plates. Compounds which hydrolized easily were collected, after the second distillation, directly in the cell in which their spectra were recorded. Steps were taken to prevent moisture from entering the cell.

$Cl_3SiCH_2CH_2Cl$ (b. p. 151.5° at 749mm) $\Delta\nu$ cm^{-1}: 163 (7), 191 (6), 228 (4*), 241 (3*), 271 (1), 301 (9), 396 (3), 448 (2*), 470 (10*), 575 (3 b**), 601 (3 b**), 647 (3), 722 (8), 761 (7), 782 (1), 1002 (1*), 1025 (3 b*), 1117 (2), 1183 (4), 1269 (2), 1303 (4), 1391 (3b), 1454 (4), 2910 (6), 2940 (3), 2967 (6), 3006 (3).

$Cl_3CCH_2CH_2Cl$ (b. p. 156.5° at 757.7mm) $\Delta\nu$ cm^{-1}: 222 (6), 249 (8), 341 (6), 356 (5), 385 (10), 440 (2db), 531 (4), 570 (9), 703 (4*), 724 (9*), 800 (4), 828 (8), 877 (1), 907 (1), 1032 (6), 1071 (7), 1114 (1), 1179 (2), 1253 (2), 1285 (4*), 1315 (2*), 1347 (1), 1432 (6*), 1453 (4*), 2943 (10), 2977 (10), 3020 (2).

$CH_3CHClCH_3$ (b. p. 34.2° at 737.3mm) $\Delta\nu$ cm^{-1}: 324 (3), 339 (6), 426 (4), 612 (10 b), 887 (6), 933 (0), 1064 (6), 1130 (3), 1162 (2), 1195 (0), 1225 (0), 1260 (4), 1330 (2), 1390 (2), 1448 (8 b), 2734 (3), 2868 (6), 2917 (9*s), 2936 (10* s), 2955 (6*s), 2976 (5**), 2992 (5**).

$(CH_3)_3SiCHClCH_3$ (b. p. 117.1° at 758.7 mm) $\Delta\nu$ cm^{-1}: 202 (6*), 216 (6*), 232 (6*), 279 (3), 304 (2), 388 (5), 423 (0), 561 (10), 628 (5), 695 (5*), 713 (6*), 756 (3), 788 (1), 825 (0*), 846 (3*), 865 (1*), 879 (0), 925 (0), 958 (3), 1018 (2), 1050 (0), 1079 (3), 1179 (3), 1240 (0), 1255 (5*), 1267 (5*), 1415 (4), 1445 (4*), 1463 (5*), 2726 (2), 2899 (10*b), 2921 (6*b), 2965 (10** b), 2986 (1**).

$CH_3SiCH_2CH_2Cl$ (b. p. 60° at 745.7mm) $\Delta\nu$ cm^{-1}: 176 (1), 244 (6), 257 (0), 489 (4), 582 (9), 610 (6*), 622 (6*), 690 (9), 731 (0), 746 (1), 753 (6*), 764 (6*), 815 (2), 871 (2), 944 (5), 960 (0), 1107 (3), 1180 (2), 1257 (3), 1378 (4*), 1434 (4*), 2156 (10 band), 2909 (7* s), 2938 (6* s), 2968 (4** s), 2983 (4** s).

$CH_3CH_2CH_2Cl$ (b. p. 45.6° at 736.8mm) $\Delta\nu$ cm^{-1}: 246 (0), 295 (2), 365 (4), 426 (2), 650 (9), 728 (6), 791 (5), 858 (4), 896 (3), 1033 (5), 1063 (1), 1105 (3), 1210 (2), 1255 (3), 1288 (2), 1302 (2), 1341 (2), 1445 (6), 1462 (2), 2742 (3), 2877 (8*), 2901 (4* s), 2917 (4* s), 2938 (8* s), 2959 (9* s), 2985 (2*), 3001 (2*).

$Cl_3CCHClCH_3$ (b. p. 151.5° at 744.2 mm) $\Delta\nu$ cm^{-1}: 173 (3), 196 (5), 240 (5), 279 (5*), 291 (5*), 343 (6), 369 (7), 441 (10), 530 (0), 562 (9 s), 698 (4), 787 (7*), 806 (7*), 931 (4 s), 1017 (3), 1089 (3 s), 1113 (3 s), 1241 (4), 1304 (2), 1383 (2), 1418 (0), 1451 (4), 2875 (2), 2948 (10*), 2965 (4*), 3003 (4).

$Cl_3SiCHClCH_3$ (b. p. 136.3° at 756.8mm) $\Delta\nu$ cm^{-1}: 167 (7*), 184 (4*), 204 (7*), 262 (8), 298 (5), 383 (9), 460 (10), 592 (2*), 609 (3*), 633 (8*), 757 (7), 963 (4), 989 (0), 1018 (3), 1046 (0), 1078 (3), 1180 (4), 1226 (0), 1256 (5), 1443 (5*), 1458 (5*), 2737 (2), 2870 (4), 2899 (3 s), 2932 (10), 2980 (5).

II. Let us now explain some features of one of the β-haloalkylsilanes viewed as a dynamic system, e.g. the compound $Cl_3Si-CH_2CH_2-Cl$, which is the most stable one as regards β-elimination. We note, first of all, that due to the action of the neighboring highly electronegative chlorine atoms**, the C−H linkages of the methylene groups experience not a decrease in electron density*** (promoting formation of protons) but, on the contrary, a very considerable increase in electron density, i.e., a shortening of the interatomic distance of the C−H linkages, an increase in their energies, and hence an increase in their vibration frequencies. The result is that the group $-CH_2CH_2-$ tightens up, as it were, and becomes more consolidated. This is clearly borne out by experimental spectroscopic data. In the compound $Cl_3Si-CH_2CH_2-Cl$, the frequencies of both methylene groups are in fact considerably higher (although not to the same degree) than the frequencies of methylene groups of normal paraffins. This is quite understandable: one of the methylene groups is more exposed to the influence

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* The intensities are expressed on the visual scale ranging from 0 to 10. The symbols attached to the intensities are: 'b' - broad line, 's' - sharp line, 'db' - double line. Lines denoted by stars (*) are situated in the background by comparison with neighboring lines which are denoted by an equal number of stars.

** It will be convenient here to quote the scale of electronegativity (according to Gordi) for the atoms which are of interest in connection with the present investigation, as well as for some other atoms, included for the purpose of comparison:

Al	Ge	Sn	Si	H	C	Cl	O	F
1.5	1.7	1.7	1.8	2.13	2.55	2.97	3.45	3.95

*** Cf. these views and the concepts of the English school (in relation to β-elimination) discussed in the paper [11].

of the single chlorine atom at the end of the chain, while the other group is influenced more by the three chlorine atoms of the silyl group. All these characteristic features of the dynamics of the methylene groups of the compound under consideration are illustrated very clearly by the increased vibration frequencies of the C−H bonds of these groups (the increase in these frequencies being accompanied, of course, by a corresponding shortening of the interatomic distances and by an increase in the energies of these bonds), as will be seen from the data in Table 1. A similar situation is observed in the case of the frequencies of the C−H bonds of the methylene groups in the compounds:

$$(CH_3O)_3Si-CH_2CH_2-Cl,\ Cl_3C-CH_2CH_2-Cl,\ H_3C\ CH_2-SiF_2-CH_2CH_2-Cl$$

and in others.

TABLE 1

Vibration Frequencies of C−H Bonds of Methylene Groups of Some Compounds*

Compounds	Frequency (cm^{-1})				
Normal paraffins: CH_2	2853	2908	–	–	–
$Cl_3Si-CH_2CH_2-Cl$:					
CH_2 (1st group)	–	2910	–	2967	–
CH_2 (2nd group)	–	–	2940	–	3006
$Cl_3C-CH_2CH_2-Cl$:					
CH_2 (1st group)	–	–	2943	2977	–
CH_2 (2nd group)	–	–	–	2977	3020

We thus see that in the structural element $-CH_2CH_2-$ of β-haloalkylsilanes, the C−H bonds of the methylene groups are in no way conditioned for proton formation but are, on the contrary, strongly polarized in the above sense of the word. However, this polarization of the C−H bonds under the influence of halogens is not an exclusive feature of the β-haloalkylsilanes which show a tendency to undergo the β-elimination. This feature is also found in other halogen derivatives which do not exhibit this tendency readily to eliminate ethylene (ethylenic hydrocarbons), either for reasons of structure (e.g. in halogen derivatives of methane), or on account of other factors connected with chemical structure; it is also found to a certain extent in the compound $Cl_3C-CH_2CH_2-Cl$, in α-haloalkylsilanes and in the corresponding organic compounds, etc. Without going into detail, we have shown in Table 2 the lower and upper limit of the vibration frequencies of the C−H

TABLE 2

Compounds	Frequency Limits (cm^{-1})			
Normal paraffins	2853	—	2967	—
$ClSi(CH_2CH_3)_3$ . . .	—	2882	—	2979
$Cl_2Si(CH_2CH_3)_2$ . . .	—	2885	—	2983
$Cl_2SiHCH_2CH_3$ . . .	—	2889	—	2986
$Cl_3SiCH_2CH_3$	—	2895	—	2996
$Cl_3CCH_2CH_3$	—	2888	—	3009
$CH_3CHClCH_3$	—	2868	—	2992
$CH_3SiCHClCH_3$ . . .	—	2899	—	2986
$CH_3SiH_2CH_2Cl$ . . .	—	2909	—	2983
$CH_3CH_2CH_2Cl$ . . .	—	2877	—	3001

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* See [3] in connection with the vibration frequencies of the C−H bonds in methylene and methyl groups given in this and other tables.

bonds of methine, methylene and methyl groups of some of the compounds mentioned. It is found that, under the influence of halogen atoms, both these limits are considerably higher in the case of these compounds than they are in the case of normal paraffins.*

The polarization of the C–H bonds, pointed out above, cannot therefore be regarded as the main factor conditioning the β-elimination.

III. Let us now turn to the elucidation of the carbon-halogen linkage in β-haloalkylsilanes, for example, in $Cl_3Si-CH_2CH_2-Cl$. If the carbon atom in the C–Cl linkage is a tertiary one, that is, if the atoms situated immediately around or in close proximity to the chlorine atom are carbon atoms, then the C–Cl linkage is characterized by the lowest vibration frequency, the greatest interatomic distance, and the lowest bond energy, i.e. the linkage is least polarized. Thus, the vibration frequency of the C–Cl bond in the compound $(CH_3)_3C-Cl$ is only 570 cm^{-1}. When, however, the carbon atom in the C–Cl bond changes to a secondary or primary one, i.e. if in the immediate neighborhood of the C–Cl linkage there appear hydrogen atoms of the methine, methylene or methyl groups, which are less electronegative than the carbon atom, then the polarization of the C–Cl link, as well as that of the C–H links of the above groups, increases; the vibration frequencies (and hence the energies) of all these linkages increase, the interatomic distances decrease – the displacement of the electronic system from the less electronegative hydrogen atoms toward the chlorine atoms does not occur through a release of hydrogen atoms as protons, but is the result of a consolidation of the entire electronic-nuclear system in that part of the molecule (Table 3).

TABLE 3

Vibration Frequencies of the C–Cl Bond in Certain Compounds

Compounds	Frequency (cm^{-1})
$(CH_3)_3CCl$**	570
$CH_3-CHCl-CH_3$ . . .	612
$CH_3CH_2-CHCl-CH_3$.	609
CH_3CH_2Cl**	656
$CH_3CH_2CH_2Cl$	648
$CH_3CH_2CH_2CH_2Cl$** . .	653
CH_3Cl**	710

TABLE 4

Compounds	Frequency (cm^{-1})
Normal paraffins	2967
$(CH_3)_3CCl$	2978
$(H_3CH_2C)_3CCl$	2998
CH_3Cl	3036

In order to characterize the simultaneous increase in the polarization of the C–H bonds in these compounds, we are listing, without going into detail, the upper limits of the frequencies of the C–H bonds for some of these compounds. We find that, already in the case of the compound $(CH_3)_3CCl$, this limit is essentially higher than in normal paraffins, and increases as we pass to CH_3Cl, parallel with the increase in the frequencies of the C–Cl bonds (Table 4; cf. Table 3).***

If, in the neighborhood of the chlorine atom of the C–Cl bond, there is situated a silicon atom (which is still less electronegative than the hydrogen atom) then, provided other influencing factors are absent, the polarization of the C–Cl bonds increases still further, as will be seen from the following comparison:

	C–Cl (cm^{-1})		C–Cl (cm^{-1})
$CH_3CH_2CH_2Cl$	650	$CH_3-CHCl-CH_3$	612
$CH_3SiH_2CH_2Cl$	690	$(CH_3)_3Si-CHCl-CH_3$	713

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* It may be mentioned that the vibration frequencies of the C–H bonds of each of the three groups - the methine, methylene and methyl groups - are independent of each other. Hence, depending on the position of the halogen in the molecule, the vibration frequencies of the C–H bonds of some of those groups which are situated close to it may experience a large increase, while at the same time the frequencies of the C–H bonds of other groups more remote from the halogen may increase by a small amount or remain unchanged.

** The data for these compounds are taken from [4].

*** See the note to Table 1, [4].

If in a given molecule, in addition to the one chlorine atom already present, there are other chlorine atoms or the more electronegative fluorine atoms, then these will, in their turn, facilitate a consolidation of the entire electronic-nuclear system and hence cause an increase in the vibration frequencies of both the C–H and the C–Cl bond:[*]

	C–Cl (cm^{-1})
CH_3CH_2Cl	656
$ClCH_2CH_2Cl$ (trans)	707, 754

As the number of chlorine atoms attached to one carbon atom increases, the electronic-nuclear interaction of the C–Cl bonds becomes more and more pronounced and results in the continued lowering of the symmetrical vibration frequency (due to the mutual repulsion of the chlorine atoms as they approach each other) and in the increase of the antisymmetrical vibration frequency. This is evident from the following data:

	C–Cl (cm^{-1})
CH_3Cl	710[*]
CH_2Cl_2	700, 736
$CHCl_3$	668, 761

If in a given molecule there are other chlorine atoms in the proximity of the CCl_3 group, the mutual interaction of all the C–Cl bonds is reinforced. As a result, the difference between the symmetrical and antisymmetrical vibration frequencies of the C–Cl bonds in the CCl_3 group becomes greater still, while the frequency of an individual C–Cl bond increases:

	Vibration frequency of the C–Cl bonds in the CCl_3 group (cm^{-1})	Vibration frequencies of the C–Cl bond (cm^{-1})
$Cl_3CCH_2CH_2Cl$	570, 828	724

Similar conditions are observed in relation to the Si–Cl bonds though, of course, at somewhat lower frequencies:

	Vibration frequencies of the Si–Cl bonds (cm^{-1})	Vibration frequencies of the C–Cl bond (cm^{-1})
$(C_2H_5)_3Si{-}Cl$	478	—
$(C_2H_5)_2Si{-}Cl_2$	457, 531	—
$(C_2H_5)Si{-}Cl_3$	447, 564	—
$Cl{-}CH_2CH_2{-}SiCl_3$	470, 575	722

Thus, the C–Cl bond in the compound $Cl_3Si{-}CH_2CH_2{-}Cl$ is essentially polarized as a result of several factors mentioned above. However, even this polarization is not a specific feature of β-haloalkylsilanes which tend to decompose with the elimination of ethylene (ethylene derivatives). In the chemically stable α-haloalkylsilanes the C–Cl bond is polarized to no lesser extent·

	Vibration frequencies of C–Cl bonds in CCl_3 groups	Vibration frequencies of C–Cl bond		Vibration frequencies of Si–Cl bonds	Vibration frequencies of C–Cl bond
$Cl_3C{-}CH_2CH_2{-}Cl$ . . .	570, 828	724	$Cl_3Si{-}CH_2CH_2{-}Cl$ . .	470, 575	722
$Cl_3C{-}CHCl{-}CH_3$ . . .	562, 806	787	$Cl_3Si{-}CHCl{-}CH_3$ . .	460, 592	757

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[*] See [3,b], pp. 392 528

It will be observed that a certain amount of screening of the C−Cl bond by the comparatively large electronic shell of the silicon atom from the orbital-electronic system of the three chlorine atoms of the $SiCl_3$ group has the effect that the per se high vibration frequencies of the C−Cl bond (due to its strong polarization) are somewhat lower in α- and β-haloalkylsilanes than the frequencies of the same bond in the corresponding halogen-substituted hydrocarbons.

From what has been said above, it is clear that as a result of the substitution in the compound $Cl_3Si{-}CHCl{-}CH_3$ of the $SiCl_3$ group by $Si(CH_3)_3$, the polarization of the C−Cl bond is somewhat lowered, i.e. its vibration frequency decreases by a small amount, the interatomic distance increases, and the bond energy decreases.

IV. The essential element in the dynamic structure of the molecule of $X_3Si{-}CH_2CH_2{-}Cl$ is the group $X_3Si{-}C{-}$. First of all, it must be stressed that the Si−C bond is, from energy considerations, the weakest bond in the molecule [5]:

Bond energy (in kcal/mole)

C—H	98.2
Si—Cl . . .	87.0
C—C	81.6
C—Cl . . .	78.0
Si—C . . .	57.6

The energy of the Si−C bond (as of all the other bonds) does, of course, assume different values depending on the structure of the molecules. However, these values lie near a level which is lower than the energy level of the other relevant bonds, as will be seen from the data in Table 5 [6].

TABLE 5

Bond Energy of the Si−C Bond in Different Compounds (in kcal/mole)

Compound	Bond energy	Compound	Bond energy	Compound	Bond energy
$(CH_3)_2SiH_2$ . . .	72	$(C_2H_5)SiH_3$ . . .	61	iso-$C_4H_9SiH_3$ . .	56
$(CH_3)_3SiH$	74	$(C_2H_5)_2SiH_2$ . .	65	n-$C_4H_9SiH_3$ . .	56
$(CH_3)_4Si$	72	$(C_2H_5)_3SiH$ . . .	63	$CH_2{=}CHSiH_3$.	63
—	—	$(C_2H_5)_4Si$	60	$(CH_3)_2Si(n\text{-}C_3H_7)_2$	61

Of essential significance in connection with our problem is the fact that the energy of the Si−C bond is considerably lower as compared with the energies of the C−C and the Si−Cl bonds which are 81.6 and 87.0 kcal/mole, respectively. The second important factor in the structural element $X_3Si{-}C{-}$ is the polarization of the Si−X bonds, particularly when X = Cl. As a result of the large difference in the electronegativities of the silicon and chlorine atoms (1.8 and 2.97, respectively), the electron shell of the silicon atom is strongly deformed, and the outer electronic orbital system of the silicon atom through which the latter is linked to the three chlorine atoms is displaced toward the chlorine atoms, with the result that the amount of screening of the positive charge on its nucleus is considerably reduced. Since in α-haloalkylsilanes ($Cl_3Si{-}CHCl{-}CH_3$ and others) the C−Cl bond is situated closer to the $SiCl_3$ group (than in the β-haloalkylsilane under consideration), the chlorine atom of this bond opposes more strongly the said reduction of the screening effect of the positive charge of the silicon atom in the $SiCl_3$ group than it does in β-haloalkylsilanes.

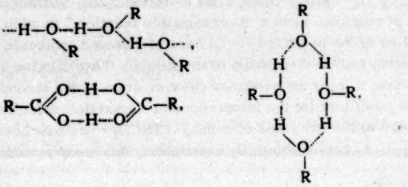
In α- and β-haloalkylsilanes in which, linked to the silicon atom, are three chlorine atoms, the C−H, C−Cl and Si−Cl bonds are essentially polarized in the sense indicated above and illustrated by the experimental evidence quoted. This means that the electronic-nuclear system of these molecules has become more compact as a result of the orbital-electronic interactions described above. Since these interactions occur between the Si−Cl bonds of the $SiCl_3$ group, on one side of the Si−C bond, and between the C−H and C−Cl bonds situated on the other side of the Si−C bond, the resultant effect is that in α- and β-haloalkylsilanes (e.g. in $Cl_3SiCHClCH_3$

and $Cl_3SiCH_2CH_2Cl$) the Si–C bond is significantly strengthened by these orbital-electronic interactions. This is manifested in the increase of the vibration frequency of this band and, therefore, in a shortening of the distance between the silicon and the carbon atom, and in an increase in energy of the bond. This strengthening of the Si–C bond is illustrated, for example, by the increase in its vibration frequency in the α-haloalkylsilane $X_3Si-CHCl-CH_3$ as X changes from a CH_3 group to chlorine: $(CH_3)_3Si-CHCl-CH_3$, 561 cm^{-1}; $Cl_3Si-CHCl-CH_3$, 633 cm^{-1}.

A similar increase in the vibration frequency of the Si–C bond (i.e. its strengthening) may, of course, be expected to be found in the β-haloalkylsilane $X_3Si-CH_2CH_2-Cl$ as we pass from X = CH_3 to X = Cl. These factore are, as we shall show below, essential for the elucidation of certain special features of the β-elimination reaction.

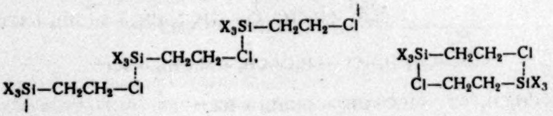
V. As we have seen, neither of the features of the dynamic structure of $X_3Si-CH_2CH_2-Cl$ discussed above appears to be a characteristic of the dynamics of this molecule as of a representative of β-haloalkylsilanes. However, one or another combination of these factors, notably in β-haloalkylsilanes, determines the greater or lesser tendency with which they undergo β-elimination reactions.

As is well known, a liquid represents a quasi-crystalline state of matter in which the orderly arrangement of molecules over more remote distances has been disturbed, while remaining more or less intact between neighboring molecules. In the latter case, the molecules arrange themselves, through various kinds of interactions, into a system possessing minimum potential energy as a result of the interactions of the force centers of the different molecules. If such intermolecular forces take the form of the hydrogen bond, then the existence of the orderly arrangements of neighboring molecules in the fluid state due to these hydrogen bonds can be demonstrated conclusively by different experimental methods, among them spectroscopy. There is no doubt that in the liquid state there exist chain and di- and polymeric ring complexes of the type:

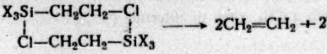


and others, in which the energy of the hydrogen bonds O .. H reaches 6-8 kcal/mole [7].

As we have seen, in the molecule $Cl_3Si-CH_2CH_2-Cl$ there exists a positive center in the form of the silicon atom, as well as a negative center in the form of the chlorine atom of the strongly polarized C–Cl bond. We may expect that, as a result of intermolecular interactions and due to a more or less preserved orderly arrangement between neighboring molecules in the liquid state, these molecules may arrange themselves in the form of a chain system or in the form of one or other ring system, such as:



and others (the dotted line indicates the direction of the intermolecular forces between neighboring molecules; X = Cl, alkyl group, etc.). The bond energy of the Si–C bond is lower than that of any of the other bonds in the molecule (57.6 kcal/mole), and is followed by that of the C–Cl bond (78 kcal/mole), while the energy of the C–C bond (81.6), and particularly that of the Si–Cl (87.0) and C–H (98.2) bonds, is large. This circumstance will have the effect that under suitable conditions (application of heat, catalytic action of nucleophilic and electrophilic reagents, etc.), neighboring molecules will interact along the dotted lines with the formation of new molecules X_3SiCl, with the elimination of ethylene, as for example:



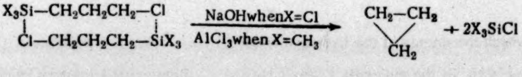
$$\begin{matrix} X_3Si{-}CH_2CH_2{-}Cl \\ Cl{-}CH_2CH_2{-}SiX_3 \end{matrix} \longrightarrow 2CH_2{=}CH_2 + 2X_3SiCl$$

We have pointed out above that the Si–C bond in β-haloalkylsilanes (as well as in α-haloalkylsilanes) becomes stronger as the group X in the compound $X_3Si-CH_2CH_2-Cl$ changes from CH_3 to Cl; the C–Cl bond is, likewise, strengthened. As a result, the compound $Cl_3Si-CH_2CH_2-Cl$ shows greater stability toward a β-elimination by the action of heat, while the compound $(CH_3)_3Si-CH_2CH_2-Cl$ undergoes the same reaction quite easily. In the case of the first compound, through the application of heat under reduced pressure in the presence of catalytic amounts of $AlCl_3$ or quinoline, dehydrochlorination takes place preferentially:

$$Cl_3Si{-}CH_2CH_2{-}Cl \rightarrow Cl_3Si{-}CH{=}CH_2 + HCl.$$

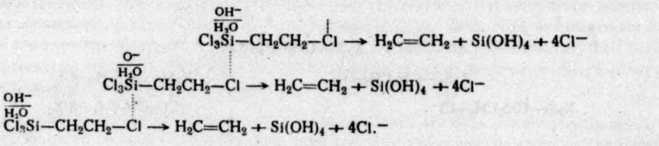
VI. It is clear that when the chlorine atom in the C–Cl bond is replaced by the silyl group $SiCl_3$, the conditions leading to a β-elimination in the molecule of $Cl_3Si-CH_2CH_2-SiCl_3$ will be absent because the intermolecular interactions described above will no longer be possible. Conditions sufficient to bring about a β-elimination will, likewise, be absent from the same sites in the molecule if the silicon atom is replaced by a carbon atom, as in the compound $Cl_3C-CH_2CH_2-Cl$: in place of the weak Si–C bond in the molecule, we now have the strong bond C–C.

In α-haloalkylsilanes, e.g. in $Cl_3Si-CHCl-CH_3$, $(CH_3)_3Si-CHCl-CH_3$, there is no structural element similar to the group $-CH_2CH_2-$ which could, after a corresponding rearrangement of its electronic system, be eliminated in the form of ethylene, as in a β-elimination reaction. In addition, a possible attack of the silicon atom by the chlorine atom of the polarized C–Cl bond of a second molecule is prevented in this case by the presence of a chlorine atom in the α-position to the silicon. This chlorine atom exerts a screening effect on the silicon atom, protecting it from the polarized chlorine atom of the second molecule. By contrast, in γ-haloalkylsilanes, all the conditions for the intermolecular interaction described above are preserved, with the sole exception that instead of the structural element $-CH_2CH_2-$ we now have in the molecule of $X_3Si-(CH_2)_3-Cl$ the group $-CH_2CH_2CH_2-$. As can be shown by experiment, this group is, indeed, eliminated as cyclopropane:[*]



At the same time, γ-chloropropyltrichlorosilane can, under given conditions, undergo dehydrochlorination with the formation of $Cl_3Si=CH-CH_3$ and $Cl_3Si-CH_2CH=CH_2$ [8].

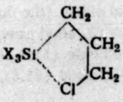
VII. The action of aqueous NaOH (nucleophilic reagent) on a β-haloalkylsilane leads to a vigorous β-elimination reaction:



$$\begin{matrix} \overset{OH^-}{\overline{H_2O}}\; Cl_3Si{-}CH_2CH_2{-}Cl \rightarrow H_2C{=}CH_2 + Si(OH)_4 + 4Cl^- \\ \overset{O^-}{\overline{H_2O}}\; Cl_3Si{-}CH_2CH_2{-}Cl \rightarrow H_2C{=}CH_2 + Si(OH)_4 + 4Cl^- \\ \overset{OH^-}{\overline{H_2O}}\; Cl_3Si{-}CH_2CH_2{-}Cl \rightarrow H_2C{=}CH_2 + Si(OH)_4 + 4Cl^-. \end{matrix}$$

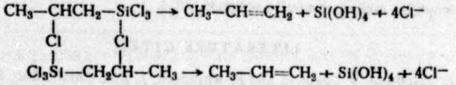
---

[*] It is possible that this takes place by the very same mechanism with a single molecule, attended by a corresponding bending of the latter. There are also other possible factors which may, in this case, bring about the elimination of cyclopropane instead of propylene. Such questions are, however, irrelevant in relation to the problem under consideration and to the interpretation given.



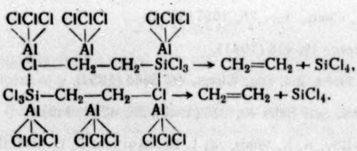
The attack of the silicon atom by the highly polarized hydroxyl ions, conditioned by the high affinity of the silicon atom for the oxygen atom, and the subsequent rearrangement of the electronic system of the molecule lead quite naturally to the elimination of ethylene and the formation of chlorine ions and $Si(OH)_4$.

The foregoing reaction may take place not only via the chain mechanism, but also via the dimeric ring complex, with the elimination of ethylene or, in the case of other molecules, of other olefins, e.g.:



$$\begin{array}{l}
\mathrm{CH_3{-}\underset{|}{C}HCH_2{-}\underset{|}{S}iCl_3 \rightarrow CH_3{-}CH{=}CH_2 + Si(OH)_4 + 4Cl^-} \\
\mathrm{\quad\ \ Cl \qquad\quad Cl} \\
\mathrm{Cl_3\overset{|}{S}i{-}CH_2\overset{|}{C}H{-}CH_3 \rightarrow CH_3{-}CH{=}CH_2 + Si(OH)_4 + 4Cl^-}
\end{array}$$

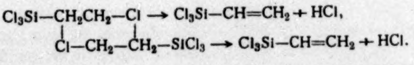
VIII. The electrophilic reagent $AlCl_3$ represents a strongly polarized molecule: the difference between the electronegativities of the aluminum atom (1.5) and the chlorine atom (2.97) is quite considerable and larger than that between the silicon atom (1.8) and the chlorine atom (2.97). The positive charge on the aluminum atom in $AlCl_3$, as well as that on the silicon atom in the group $SiCl_3$, is strongly de-screened. The catalytic action of $AlCl_3$ in β-elimination reactions may consist in the following. As we have seen, nearly all the bonds in the molecule of $Cl_3Si-CH_2CH_2-Cl$ (as also in other β-haloalkylsilanes) are characterized by high electron density, i.e. the nuclei of the atoms are drawn deep into the interior of the orbital-electronic system of the molecule. The molecule of $AlCl_3$ orients itself with its positive end toward the polarized bonds of the chain or ring complexes (for brevity, let us consider the ring complex):



$$\begin{array}{l}
\mathrm{\ ClClCl\ \ ClClCl\qquad ClClCl} \\
\mathrm{\ \ \ Al\qquad\ Al\qquad\quad\ Al} \\
\mathrm{Cl{-}CH_2{-}CH_2{-}SiCl_3 \rightarrow CH_2{=}CH_2 + SiCl_4,} \\
\mathrm{Cl_3Si{-}CH_2{-}CH_2{-}Cl \rightarrow CH_2{=}CH_2 + SiCl_4.} \\
\mathrm{\ \ \ Al\qquad\ Al\qquad\quad\ Al} \\
\mathrm{\ ClClCl\ \ ClClCl\qquad ClClCl}
\end{array}$$

The aluminum atoms of the $AlCl_3$ molecules tend to pull the electronic system of the silane molecules toward themselves. The silicon atom, being the weakest site in the molecule (as regards its ability to attract the outer orbital electronic system), the result is that there is a further reduction in the amount of screening of its positive nucleus. This allows the interaction of the Si ... Cl bonds to become intensified, finally leading to β-elimination reactions, as discussed above.

However, parallel with the β-elimination by $AlCl_3$, in compounds similar to $Cl_3Si-CH_2CH_2-Cl$, we can also observe dehydrochlorination reactions brought about by similar intermolecular interactions. By promoting the ionization of the hydrogen atoms of the C–H bonds of the methylene groups, $AlCl_3$ facilitates the formation of strong intermolecular links H ... Cl which are, on the basis of other experimental evidence [9], but another form of hydrogen bonds:



$$\begin{array}{l}
\mathrm{Cl_3Si{-}CH_2\underset{|}{C}H_2{-}\underset{|}{C}l \rightarrow Cl_3Si{-}CH{=}CH_2 + HCl,} \\
\mathrm{\qquad\quad Cl{-}CH_2{-}CH_2{-}SiCl_3 \rightarrow Cl_3Si{-}CH{=}CH_2 + HCl.}
\end{array}$$

Experiment shows that in the case of $Cl_3Si-CH_2CH_2-Cl$ and other compounds, the tendency to undergo a β-elimination reaction or dehydrochlorination depends to a considerable extent on the experimental conditions [10].

As we now see, dehydrochlorination and other reactions mentioned above are quite similar in this respect to β-elimination reactions. They are conditioned not only by the structural features of the molecule as such, but also by intermolecular interactions similar to those discussed above. However, these problems are beyond the scope of this paper.

In the experimental spectroscopic work, the authors were assisted by M. F. Zulina, while N N. Mkhitaryan has assisted in the preparation of the compounds examined.

SUMMARY

1. On the basis of a spectroscopic investigation of the compound $Cl_3Si-CH_2CH_2-Cl$ and of other halogen derivatives of hydrocarbons and of organosilicon compounds, the authors have shown that the β-elimination reaction of β-haloalkylsilanes is a consequence of the specific structure of these molecules.

2. Spectroscopic analysis of this specific structure leads to the conclusion that of essential importance for the β-elimination process are the forces resulting from the intermolecular interactions Si... Cl, and it is along the lines of action of these forces that the said elimination reaction can take place under suitable conditions (heating, action of nucleophilic and electrophilic reagents, etc.).

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INVESTIGATION OF THE INTERACTION OF CHLOROSULFONIC ACID WITH AROMATIC COMPOUNDS

III. DI- AND POLYSULFONATION REACTIONS DURING SULFONATION OF ACETANILIDE

B. G. Yasnitsky

In previous papers we have considered the mechanism and kinetics of reactions which lead to the formation of monosulfochlorides as a result of the action of chlorosulfonic acid on some aromatic compounds [1,2]. In the present communication, we are considering the processes of di- and polysulfonation which take place during the chlorosulfonation of acetanilide and their effect on the yield of monosulfochloride.

Acetanilide was chosen for these experiments because its sulfonation with chlorosulfonic acid proceeds rapidly and completely when the latter is used in excess. Also, no detectable amounts of sulfonates are formed during the reaction, various sulfonic acids and sulfochlorides being the main products of the reaction.

EXPERIMENTAL

The experimental technique did not differ from that described previously [1]. The amounts of reagents used were 6.75 g of acetanilide, m.p. 114.7°, and 28.2 g of 98.3% chlorosulfonic acid (i.e. 1:4.76 moles).

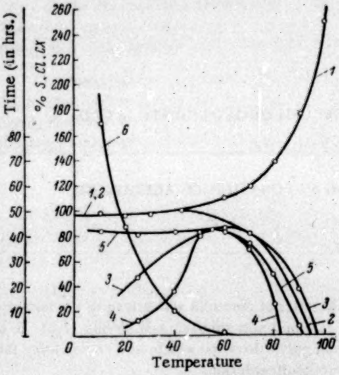
In order to determine the unreacted acetanilide in the reaction mixture, a sample of the latter was submitted to hydrolysis by boiling with 15% caustic soda for two hours and subsequently extracting the aniline with benzene. The aniline was extracted from its benzene solution with 5% hydrochloric acid and was then determined by diazotization.

The sulfonated reaction mixture, i.e. the mother liquor and the residue, obtained after dissolving the sulfonated mass with water, was analyzed as follows. The amount of organic sulfur, i.e. sulfur which has entered the molecule of the organic compound in the form of the sulfonic or sulfochloride groups, was determined by the difference between "total" sulfur, determined by the method of Messinger, and "mineral" sulfur, estimated by precipitation with barium chloride. The "organic" chlorine was determined as the difference between "total" chlorine by Volhard's method after hydrolysis of the sample, and "mineral" chlorine determined by Volhard's method in the original sample.

Monosulfochlorides were determined from the weight of the dry residue after recrystallization from dichloroethane to constant melting point and to constant chlorine and sulfur content of 15.2% and 13.7%, respectively, taking into account the calculated losses due to recrystallization.

The experimental conditions and results are shown in the figure. From Curve (1) it will be seen that the number of sulfur-containing groups per molecule is little affected by temperature between 0-40°, and on the average there is one such group per molecule. In special experiments it was shown that 2 hours appear to be a sufficiently long period for attaining maximum sulfonation at these temperatures. As no sulfonates or any unreacted acetanilide have been detected in the reaction products when the experiments were carried out at temperatures from 0 to 100°, over periods of 2 hours, it can be assumed that practically no disulfo-derivatives are formed at temperatures up to 40°. The steep rise of Curve (1) in the interval 40-100° to 250% indicates rapid formation of di- and trisulfo-derivatives with rise in temperature (see figure).

In order to simplify the calculation let us assume that each point on the curve in this interval corresponds to a mixture consisting of sulfonates of two kinds only: mono- and disulfonates or di- and trisulfonates. Although this assumption introduces a negligible error, it allows us to calculate the amount of each of these products



Analysis of chlorosulfonation of acetanilide.*
1) Content of "organic" sulfur in sulfonated mass (in % of theoretical for full conversion of acetanilide into monosulfo derivative); 2) monosulfoderivative (in %); 3) content of "organic" chlorine in sulfonated mass (in % of theoretical for full conversion of acetanilide into monosulfochloride); 4) yield of acetanilide monosulfochloride; 5) yield of monosulfochloride in the "equilibrium" mixture; 6) time required to attain "equilibrium".

according to the formula $a = Xn + (100 - X)m$, where a is the percentage of organic sulfur in the reaction products, n is the calculated percentage of sulfur in the monosulfo derivatives, m is the calculated percentage of sulfur in the disulfo derivatives, and X is the molar percentage of the monosulfo-derivatives.

The data calculated have been used to construct Curve (2) which gives the variation of the amount of monosulfo derivative with temperature. From the position of the curve, it may be concluded that in the case where the final product of chlorosulfonation is p-acetaminobenzosulfochloride, an increase in the reaction temperature above 40° leads to a sharp decrease of the yield of the main product with a corresponding increase in polysulfo derivatives. It will also be seen that, for this very reason, the yield of monosulfochloride at a temperature of 70° recommended by some authors (see, for example, [3-5]), cannot be expected to exceed 80%. However, there are other causes which contribute to this decrease of the yield at high temperatures. We have shown [1] that the yield of acetanilide monosulfochloride depends, apart from the temperature and length of chlorosulfonation, mainly on the composition of the reaction mass and partly on the ratio of chlorosulfonic and sulfuric acid in the "final" state of the system (see also [6-8]). The progress of di- and polysulfonation processes at high temperatures is connected with a decrease in the absolute and relative amounts of chlorosulfonic acid. This causes the equilibrium in the system sulfonic acid ⇌ sulfochloride to shift in the direction leading to a decrease in the amount of sulfochloride (i.e. organically combined chlorine). In addition, as the temperature rises the irreversible decomposition of acetanilide sulfochloride under the action of sulfuric acid becomes more and more important, leading to the evolution of an additional quantity of hydrogen chloride from the reaction mixture [1,2]. This is clearly seen from a comparison of the downward slope of the curves, giving the yield of sulfochloride after having reached a maximum, depending on the length of the experimental period at 25 and 40°. It is quite obvious that this drop in the yield of sulfochloride has no connection with the disulfonation process, since it also occurs when the amount of "organic" sulfur remains practically unchanged.

Let us examine the effect of the processes mentioned on the amount of "organic" chlorine and on the yield of monosulfochloride (Curves 3 and 4). When these curves are contrasted with the corresponding curves in Fig. 1 in communication [1] it will be seen that the initial rise of the curves is due to incomplete chlorosulfonation, i.e. due to the equilibrium: sulfonic acid ⇌ sulfochloride not having been attained at the end of the period chosen, namely, two hours. The dropping branches of the curves correspond to those temperatures (60-100°) at which the chlorosulfonation equilibrium (more accurately "pseudo-equilibrium" [2]) is reached within a considerably shorter period than 2 hours. The downward incline of the curves in this interval appears to be mainly the result of di- and polysulfonation and of the decrease in the concentration of chlorosulfonic acid due to these processes, as well as to the irreversible decomposition of sulfochlorides. Evidently, the shift in the equilibrium due to the difference of the temperature coefficients of the reaction velocities in both directions is of no great significance. As has been shown by A. A. Spryskov and Yu. L. Kuzmina [8b] for p-dichlorbenzosulfonic acid, this is primarily due to the fact that the equilibrium constant does not vary substantially with temperature. Secondly, it will be seen from the position of Curve (5) that in the temperature interval of 10-50°, when there is practically no disulfonation taking place and when decomposition of sulfochlorides proceeds at a very slow rate, the maximum yield of sulfochloride determined within the limits of analytical accuracy is practically independent of the reaction temperature. Curve (4), which gives the yield of monosulfochloride, is inclined more steeply than Curve (3), which gives the "organic" chlorine content of the sulfonated mass. This shows that a proportion of the sulfochloride groups is contained in the polysulfo derivatives.

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* Curves 1-4 refer to experiments of 2 hours' duration.

As will be seen from Curve (5), the maximum yield of sulfochloride (80-85%) may be obtained at chlorosulfonation temperatures not higher than 60-63°, using reagents of the purity indicated. At higher temperatures there is a sharp decrease of the yield due to the causes discussed above. When the reaction is carried out at temperatures below 60°, the yield is not affected substantially, but since the duration of the reaction period increases sharply with decrease of temperature (Curve 6), it would be unreasonable to carry out the reaction at such temperatures. Thus, the optimum temperature for the reaction lies between 55 and 60°, the maximum yield being attained after 1-1½ hours, which is also in accordance with the findings of a number of previous workers [9-11].

It must also be mentioned that the products of polysulfonation, after dilution of the sulfonated mass with water, exist both in solution and partly as precipitates in the residue, together with p-acetaminobenzosulfochloride. For this reason, the determination of monosulfochloride from the weight of the dry residue or from the amount of organic chlorine expressed as monosulfochloride – a method used by some workers and also one used in practice – does not always give the actual content of the product sought. Thus, the product obtained by chlorosulfonation of acetanilide at 70°, appears to consist of sufficiently pure monosulfochloride. Its percentage yields determined by diazotization (67.7%), from the weight of the dry compound (67.0%), from the amount of "organic" chlorine (66.5%), and from the "organic" sulfur (68.0%) are sufficiently close from the practical point of view. The percentage contents of sulfur (13.9%) and chlorine (15.1%) in the product are likewise sufficiently close to the theoretical (13.7 and 15.2%). However, the dry product obtained at 90° gives quite different results, depending on the analytical method used; its chlorine content is found to be 17.1% and the sulfur content 20.9%, results which are considerably higher than the calculated percentages for monosulfochloride.

During chlorosulfonation of acetanilide as carried out in actual practice it is, therefore, necessary to take into account di- and polysulfonation reactions, as such reactions appear to be among the chief factors affecting sharply the yield of p-acetaminobenzosulfochloride and the purity of the product obtained.

SUMMARY

1. It has been shown that, in the course of chlorosulfonation of acetanilide at temperatures above 40°, formation of di- and polysulfo derivatives takes place. Di- and polysulfonation reactions bring about a substantial decrease in the yield of p-acetaminobenzosulfochloride as a result of transformation of a part of the reaction product into compounds of higher degree of sulfonation, and also due to the lowering of the concentration of chlorosulfonic acid as a result of polysulfonation reactions.

2. Experimental evidence has been provided, confirming the statement expressed previously that the temperature of 55-60° appears to be the optimum temperature for the chlorosulfonation of acetanilide. It has been shown that at lower temperatures the yield in the equilibrium mixture remains practically unchanged, but, on the other hand, the length of the reaction period increases markedly. A rise in temperature brings about a sharp lowering of the yield of sulfochloride as a result of disulfonation reactions and of the decomposition of the sulfochloride.

3. p-Acetaminobenzosulfochloride, obtained by chlorosulfonation at high temperatures (above 70°), contains considerable amounts of disulfo derivatives and, for this reason, cannot be determined analytically from an estimation of organically bound chlorine.

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TETRAACYLOXYSILANES IN ORGANIC SYNTHESES

VI. ACYLOXYSILANES FROM MONOBASIC ORGANIC ACIDS IN THE SYNTHESIS OF KETONES OF THE INDOLE AND PYRROLE SERIES

Yu. K. Yuryev and G. B. Elyakov

Acylation of indole was carried out by Ciamician and Zatti [1]: 1,3-diacetylindole, prepared by reaction of acetic anhydride on indole was easily hydrolyzed by boiling with soda, with the formation of 3-acetoindole. Later, Oddo and Sessa [2] obtained ketones of the indole series by the action of acid chlorides on indolyl magnesium iodide.

Saxton [3] obtained 3-acetoindole in 55-60% yield by acylation of indole with acetic anhydride in the presence of acetic acid. The 1,3-diacetylindole formed was hydrolyzed with alcoholic alkali with quantitative yield of 3-acetoindole.

Acylation of indole by the Gustavsson-Friedel-Crafts reaction was investigated by Borscher and Groth, who found that in the presence of aluminum chloride, in carbon disulfide as medium, substituted indoles can be acylated by acetic anhydride or acetyl chloride in positions 2 or 3 or, if these are occupied already, in the benzene ring. In most cases the yields are good.

Ketones of the pyrrole series are obtained by methods similar to those used in the preparation of 3-indolyl ketones. Ciamician and Dennstedt [5] have acylated pyrrole by the action of acetic anhydride in the presence of sodium acetate.* The yield of 2-acetylpyrrole in this reaction did not exceed 20-25%. Later Dennstedt and Zimmermann [7] modified the acylation procedure, using zinc chloride as catalyst. This did not produce any marked improvement in the yields, but shortened the reaction time.

By a method similar to that used in the preparation of 3-indolyl ketones, it is possible to prepare ketones of the pyrrole series by the action of acid chlorides or acid anhydrides on pyrrylmagnesium iodide [8,9], with yields of the corresponding ketones of 50-60%. A good method of preparation of pyrryl ketones in yields of 50-60% has been evolved by V. V. Chelintsev and A. P. Terentyev [10]. By the action of complex esters of acids on pyrrylmagnesium bromide, the corresponding ketones are easily prepared. In this way 2-acetopyrrole, 2-propiopyrrole and 2-butyropyrrole have been obtained.

The majority of ketones of the pyrrole series, with various substituents in the pyrrole nucleus, have been obtained by the Hoesch reaction [11,12,13], as well as by the Gustavsson-Friedel-Crafts reaction [14].

In previous papers we have shown that mixed anhydrides of silicic and organic acids (tetraacyloxysilanes) can be used as acylating agents in the preparation of ketones of the thiophene [15] and selenophene series [16,17].

For this reason we have attempted to carry out the acylation of indole and pyrrole with these readily accessible and easily prepared acylating agents. In the course of the acylation of indole with tetraacetoxysilane under various conditions in the presence of various catalysts, we have established that either no reaction takes place or acylation occurs – in the presence of efficient condensing agents – with the formation of considerable amounts of tarry matter. Maximum yield of 3-acetoindole (21%, based on the indole) was obtained by acylation of indole with tetraacetoxysilane in the presence of lead chloride, using benzene with a small quantity of added dioxan as reaction medium:

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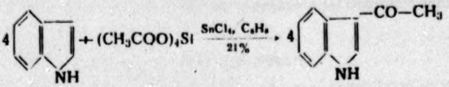
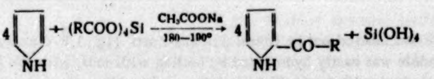
* α-Acetylpyrrole was first prepared by Schiff [6] who erroneously assumed it to be N-Acetylpyrrole.



In the course of the acylation of pyrrole with acyloxysilanes of various aliphatic acids, we have found that the best catalyst for this reaction is anhydrous sodium acetate.

Although, in the course of this acylation of pyrrole, small amounts of 3-acetopyrrole are formed, the reaction proceeds rapidly and at a lower temperature than if the sodium salt of the acid,of which the acyloxysilane consists, is used. Substituting sodium acetate by potassium acetate does not increase the yield of the ketones.



$R = CH_3,\ C_2H_5,\ C_3H_7,\ iso\text{-}C_4H_9,\ C_5H_{11}.$

In this manner, we have obtained 2-acetopyrrole, 2-propiopyrrole, 2-n-butyropyrrole, 2-isovaleropyrrole, and 2-n-capropyrrole in yields of 40-50%, based on the pyrrole taken (unreacted pyrrole is recovered pure from the reaction mixture).

EXPERIMENTAL

3-Acetoindole. 200 ml of dry benzene, 12 g (0.2 mole) of acetic acid, and 8.5 g (0.05 mole) of silicon tetrachloride were weighed into a three-necked flask with a stirrer, reflux condenser and dropping funnel, and warmed on a water bath until the evolution of hydrogen chloride ceased. The flask was then cooled, 13 g (0.05 mole) of anhydrous lead chloride added, and dry air passed through for 30 minutes. 11.7 g (0.1 mole) of indole in 30 ml of benzene and 2 ml of dioxan were added dropwise at 20°. A viscous mass formed which made stirring difficult. Heating was continued on a water bath for three hours, the flask was then cooled and the reaction mixture digested with 150 ml of concentrated caustic potash. The mixture was stirred for three hours and the benzene and unreacted indole (1.7 g) then steam distilled. The hot residue was filtered through a cotton cloth. The filtrate was acidified slightly and extracted with ether for 10 hours in a continuous extractor. The ether extract was dried. After removal of the ether, 2.5 g of 3-acetoindole, m.p. 191° (from alcohol) was obtained (21% of theoretical, based on the indole taken). The m.p. of a mixture of the substance with an authentic sample was not depressed. Literature data for 3-acetoindole: m.p. 191° [3].

Ketones of the Pyrrole Series

Experimental method. 200 ml of dry benzene, 0.7-1 mole of a dibasic organic acid, and 0.175-0.25 mole of silicon tetrachloride were put into a two-necked flask (300 ml) with a reflux condenser and stirrer, and warmed on a water bath until the evolution of hydrogen chloride ceased. Benzene was removed in vacuum at 30-40° on a water bath, and to the syrupy tetracyloxysilane were added 0.4 mole of anhydrous sodium acetate and 0.1-0.2 mole of freshly distilled pyrrole; the flask was fitted with a reflux condenser and thermometer,and the mixture heated on an oil bath at 180° (in the reaction mixture) for 6 hours.

To the reaction mass, which solidified on cooling, 50-80 ml of concentrated sodium hydroxide was added gradually while cooling with ice. The solution was transferred into a larger flask and steam distilled. The distillate was saturated with sodium chloride and repeatedly extracted with ether, the ether extracts dried with fused sodium sulfate, the ether removed, and the residue distilled in vacuum. At first, the unchanged pyrrole came over, followed by the ketone which was recrystallized from dilute alcohol or water.

2-Acetopyrrole. From 48 g of acetic acid, 34 g of silicon tetrachloride, 6.7 g of pyrrole and 10 g of sodium acetate was obtained 3.7 g (34%) of methyl-2-pyrrylketone, m.p. 89-90°. After recrystallization from water, 2-acetopyrrole melted at 90°.

Found %: N 13.15, 13.33. C_6H_7ON. Calculated %: N 12.84.

On acylation of pyrrole with tetraacetyloxysilane in the presence of anhydrous lead chloride, in anhydrous benzene (as described above for 3-acetoindole), 2-acetopyrrole was also prepared in a yield of only 17%. When anhydrous zinc chloride was used under otherwise unchanged conditions, the yield of 2-acetopyrrole was 24% of theoretical. Literature data for 2-acetopyrrole: m.p. 90° [5,9].

2-Propiopyrrole. From 60 g of propionic acid, 34 g silicon tetrachloride, 13.4 g of pyrrole and 20 g of sodium acetate was obtained 7.9 g of pyrrole and 5.5 g of ketone (54% of theoretical, based on pyrrole) in the form of a light yellow oil, distilling at 153-155° (73 mm) and crystallizing on cooling. After recrystallization from aqueous alcohol the 2-propiopyrrole had m.p. 52-52.3°.

Found %: N 11.60, 11.62. C_7H_9ON. Calculated %: N 11.42.
Literature data for 2-propiopyrrole: m.p. 52° [9], 52.5° [7].

2-n-Butyropyrrole. Reacting 88 g of butyric acid, 42.5 g of silicon tetrachloride, 13.4 g of pyrrole and 20 g of sodium acetate gave 5.6 g of unchanged pyrrole and 6.7 g of the ketone (50% of theoretical, based on pyrrole), distilling at 119° (9 mm) and crystallizing on cooling. After recrystallization from aqueous alcohol, 2-n-butyropyrrole melted at 47.5-48.2°.

Found %: N 9.86, 10.06. $C_8H_{11}ON$. Calculated %: N 10.21.
Literature: m.p. 48° [9], 48.5° [7].

2-Isovaleropyrrole. From 72 g of isovaleric acid, 30.6 g of silicon tetrachloride, 13.4 g of pyrrole and 20 g of sodium n-valerate was obtained 11 g of unchanged pyrrole and 2.2 g of the ketone (41% of theoretical, based on the pyrrole taken). M.p. 133-134° (15 mm), n_D^{20} 1.5285, d_4^{20} 0.9949, MR_D 46.86. $C_9H_{13}ONF_2$. Calc. 45.52.

Found %: N 9.22, 9.32. $C_9H_{13}ON$. Calculated %: N 9.30.
2-Isovaleropyrrole has not been described in the literature.

2-n-Capropyrrole. Reacting 82 g of caproic acid, 30.6 g of silicon tetrachloride, 13.4 g of pyrrole and 20 g of sodium acetate gave 7.2 g of unchanged pyrrole and 7 g of the ketone (47% of theoretical, based on the pyrrole taken) which distilled at 140-142° (8 mm) and crystallized on standing for a week. After redistillation the ketone crystallized immediately, m.p. 35-37°.

Found %: N 8.71, 8.73. $C_{10}H_{15}ON$. Calculated %: N 8.48.
The semicarbazone forms a crystalline monohydrate melting at 113-114°.
Found %: N 23.46, 23.49. $C_{11}H_{18}ON_4 \cdot H_2O$. Calculated %: N 23.32.
2-n-Capropyrrole has not been described in the literature.

SUMMARY

1. By preparing 3-acetoindole the authors have demonstrated the possibility of acylating indole with tetraacetoxysilane in the presence of lead chloride.

2. A method has been developed for the acylation of pyrrole with tetraacyloxysilanes in the presence of sodium acetate, which may be used to prepare ketones of the pyrrole series in yields of 40-50%. Using this method, the authors have prepared 2-aceto-, 2-propio-, 2-n-butyro-, 2-isovalero-, and 2-n-capropyrrole.

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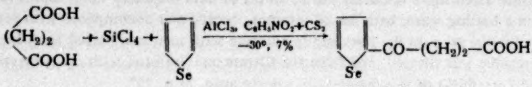
THE CHEMISTRY OF SELENOPHENE

III. ACYLOXSILANES FROM DICARBOXYLIC ACIDS AND THEIR MONOETHYL ESTERS IN THE SYNTHESIS OF KETO ACIDS OF THE SELENOPHENE SERIES

Yu. K. Yuryev, G. B. Elyakov and Z. V. Belyakova

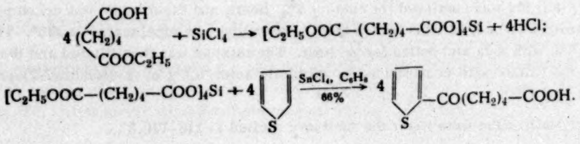
Of the keto acids of the selenophene series only one has been described in the literature, namely, o-(2,5-dimethylselenoyl-3)-benzoic acid, which has been obtained in a yield of 7% by the action of phthalic anhydride on 2,5-dimethylselenophene in the presence of aluminum chloride in carbon disulfide as reaction medium [1].

In previous communications we have described a new method for the preparation of keto acids of the benzene [2] and thiophene [3] series, using acyloxysilanes from dicarboxylic acids. Our attempt to obtain keto acids of the selenophene series by the same method did not give any positive results. When the reaction was carried out under conditions similar to those used in the preparation of keto acids of the thiophene series (in nitrobenzene, in the presence of aluminum chloride), there occurred rupture of the selenophene ring, and only at a temperature of −30°, in a mixture of nitrobenzene and carbon disulfide as reaction medium, did we succeed in obtaining β-(selenoyl-2)-propionic acid, but in small yield:



From the literature it is known that the best yields of keto acids of the thiophene series have been obtained by acylation of thiophene with ethyl ester acid chlorides of dicarboxylic acids in the presence of lead chloride [4,5]. We have, therefore, deemed it expedient to prepare acyloxysilanes from monoethyl esters of dibasic acids and to apply them for the acylation of selenophene in the presence of lead chloride.

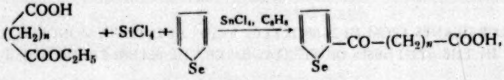
The fundamental possibility of acylating with acyloxysilanes from monoethyl esters of dibasic acids was first established in the case of the thiophene series by preparing δ-(thenoyl-2)-valeric acid. This method of acylating thiophene gives good results, the yield of the ketoacid approaching 66%.


COOH
4 (CH₂)₄
COOC₂H₅
+ SiCl₄ → [C₂H₅OOC—(CH₂)₄—COO]₄Si + 4HCl;
[C₂H₅OOC—(CH₂)₄—COO]₄Si + 4
S
SnCl₄, C₆H₆
66%
4
S
—CO(CH₂)₄—COOH.

We mention that this keto acid was prepared by us previously in 33% yield by using adipyloxysilane in the presence of aluminum chloride [3]. By using the acyloxysilane from ethyl hydrogen adipate [tetra-(δ-carbethoxy)-valeryloxysilane] and lead chloride as the condensing agent, the yield of the keto acid was almost as good as when this acid was prepared by the action of the ethyl ester-acid chloride of adipic acid (yield 70%)[4].

We have used a number of tetra-(ω-carbethoxy)-acyloxysilanes for the acylation of selenophene in the presence of anhydrous lead chloride and, without isolating the esters of the corresponding keto acids, we have hydrolyzed them by passing steam into the reaction mixture made alkaline with soda, ultimately obtaining keto acids of selenophene and of its substitution products.

In this manner we have prepared the following keto acids of the selenophene series which have not previously been described in the literature: β-(selenoyl-2)-propionic acid (20%), δ-(selenoyl-2)-valeric acid (38.5%), η-(selenoyl-2)-caprylic acid (30%), and ν-(selenoyl-2)-pelargonic acid (42%).



where n = 2, 4, 7, 8.

Lower yields of keto acids of the selenophene series are due to the comparatively low stability of the selenophene ring, which under the conditions of the reaction undergoes partial rupture, with the formation of metallic selenium.

EXPERIMENTAL

δ-(Thenoyl-2)-valeric acid. 9.6 g (0.055 mole) of ethyl hydrogen adipate, 70 ml of dry benzene, and 4.8 g (0.028 mole) of silicon tetrachloride were weighed in a 250-ml 3-necked flask provided with a mechanical stirrer, dropping funnel and reflux condenser with a calcium chloride tube, and the mixture was heated on a water bath, first at 50-60° and subsequently on a boiling water bath, until the evolution of hydrogen chloride ceased. The mixture was cooled in ice, and 4.2 g (0.05 mole) of thiophene and 6.5 g (0.025 mole) of anhydrous lead chloride in 6 ml of benzene was added, the latter dropwise. Stirring was continued at room temperature for one hour, the mixture assuming a raspberry color; an oil of dark raspberry color separated. The reaction mixture was then heated on a boiling water bath for 30 minutes, cooled and decomposed with ice. The benzene was steam-distilled and the residue in the flask made alkaline with soda and boiled for 5 hours* by passing steam through it. The residue was filtered, and from the filtrate on acidifying with concentrated hydrochloric acid, there was obtained 7 g (66%) of δ-(thenoyl-2)-valeric acid, m.p. 77°.

After recrystallization from water, the compound melted at 78-79°. The melting point of a mixture of the substance with an authentic sample of δ-(thenoyl-2)valeric acid was not depressed. Literature, m.p. 76-77° [4], 78-79° [3].

Acylation of selenophene with succinyloxysilane: β-(selenyl-2)-propionic acid. 4.72 g (0.04 mole) of succinic acid, 50 ml of nitrobenzene, and 3.4 g (0.02 mole) of silicon tetrachloride were transferred into the apparatus described above and heated on a water bath, at first at 70-80°, and subsequently on a boiling water bath, until the evolution of hydrogen chloride ceased. The solution of the acyloxysilane was cooled to room temperature, 130 ml of dry carbon disulfide was added, followed by 7.5 g (0.056 mole) of anhydrous aluminum chloride, the mixture was cooled to −30 to −40°, and 4 g (0.03 mole) of selenophene in 6 ml of nitrobenzene was added dropwise. A heavy, dark green oil separated at the bottom of the flask, and the solution assumed a turquoise color. Stirring was continued for another 3½ hours, and the mixture was decomposed with ice. Carbon disulfide was steam-distilled, nitrobenzene was distilled with steam superheated to 300°. The residue in the flask was made alkaline with soda and boiled for ½ hour. The mixture was then filtered and the keto acid was precipitated from the filtrate with concentrated hydrochloric acid. 0.5 g of β-(selenoyl-2)-propionic acid was obtained, m.p. 113° (7%).

After recrystallization from water the substance melted at 116-116.5°.

Found %: C 41.58, 41.59; H 3.70, 3.71. $C_8H_8O_3Se$. Calculated %: C 41.58; H 3.49.

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* The prolonged boiling with soda is necessary, both in this and in all the subsequent preparations of keto acids with acyloxysilanes from monoethyl esters of dibasic acids, in order to hydrolyze the carbethoxy group and to obtain the salt of the keto acid.

Acylation of Selenophene With Tetra-(ω-Carbethoxy)-Acyloxysilanes

Experimental method. Into the apparatus described above was transferred 0.06-0.02 mole of the monoethyl ester of the given dicarboxylic acid, 20-70 ml of dry benzene (depending on the amount of the reagents), and 0.03-0.005 mole of silicon tetrachloride, and the mixture was heated on a water bath until the evolution of HCl ceased. The reaction mixture was cooled in ice water, 0.015-0.008 mole anhydrous $PbCl_2$ was added, followed by a dropwise addition of 0.03-0.015 mole of selenophene in a small quantity of benzene. The mixture was stirred for 15-20 min at room temperature, heated 5-10 min on a water bath at 60-70°, cooled, and decomposed with ice. The benzene was removed with steam, and the residue in the flask was made strongly alkaline with soda, and boiled for three hours by passing superheated steam. The reaction mixture was then filtered, and from the filtrate, after acidification, a small quantity of the dicarboxylic acid, together with a small amount of the keto acid was obtained. (The ester of the keto acid was hydrolyzed only to a small extent during the 3 hours). The residue was again boiled with soda for 5 hours, filtered, and acidified with concentrated hydrochloric acid to precipitate the keto acid. By boiling the mother liquor, containing the dicarboxylic acid, for a further 3 hours, followed by fractional crystallization, it was possible to isolate an additional small quantity of the keto acid. In the case of ν-(selenoyl-2)-pelargonic acid, the residue obtained after boiling the reaction mixture with soda for 40 minutes was filtered, and the ethyl ester of the keto acid extracted from the filtrate with ether. (At the end of 40 minutes' boiling the ethyl hydrogen ester was hydrolyzed completely, whereas the ethyl ester of the keto acid was hydrolyzed only to a negligible extent). The ether extract and the residue were transferred into a flask, the ether removed, a further amount of soda added, and hydrolysis carried out by passing superheated steam for 6 hours. The hydrolyzate was filtered and the filtrate acidified to give the keto acid without the dicarboxylic acid as impurity.

We may mention that, in the case of the preparation of β-(selenoyl-2)-propionic and δ-(selenoyl-2)-valeric acids, the isolation of these acids is easier because succinic and adipic acids are sufficiently soluble in water, and a preliminary boiling of the solution, in order to remove the dicarboxylic acid, is unnecessary. The keto acids of the selenophene series recrystallized from water or aqueous alcohol.

β-(Selenoyl-2)-propionic acid. From 8.76 g of ethyl hydrogen succinate, 5.1 g of silicon tetrachloride, 3.9 g of lead chloride, and 4 g of selenophene in 70 ml of benzene, there was obtained 1.4 g of the keto acid, m.p. 114° (20%).

After recrystallization from water, the β-(selenoyl-2)-propionic acid had m.p. 116-116.5°, and no depression of the melting point of a mixture of this acid with the keto acid obtained in the previous experiment was observed.

δ-(Selenoyl-2)-valeric acid. Reacting 7 g of ethyl hydrogen adipate, 3.4 g of silicon tetrachloride, 7.8 g of lead chloride, and 4 g of selenophene in 70 ml of benzene, gave 3 g of the keto acid (38.5%), m.p. 68°. After recrystallization from water, the acid melted at 70-70.5°.

Found %: C 46.38, 46.54; H 4.73, 4.90. $C_{10}H_{12}O_3Se$. Calculated %: C 46.34; H 4.66.

η-(Selenoyl-2)-caprylic acid. From 4.32 g of ethyl hydrogen azelate, 0.85 g of silicon tetrachloride, 1.36 g of lead chloride and 2 g of selenophene in 20 ml of benzene, there was obtained 1.35 g (30%) of η-(selenoyl-2)-caprylic acid, m.p. 71°. After recrystallization from aqueous alcohol, the compound melted at 71.5-72°.

Found %: C 52.05, 52.15; H 6.17, 6.21. $C_{13}H_{18}O_3Se$. Calculated %: C 51.82; H 6.02.

ν-(Selenoyl-2)-pelargonic acid. From 4.6 g of ethyl hydrogen sebacate, 0.85 g of silicon tetrachloride, 1.36 g of lead chloride and 2 g of selenophene in 20 ml of benzene, there was obtained 2 g of ν-(selenoyl-2)-pelargonic acid, m.p. 50°. After recrystallization from aqueous alcohol, the acid melted at 50.5-51°.

Found %: C 53.67, 53.83; H 6.47, 6.58. $C_{14}H_{20}O_3Se$. Calculated %: C 53.33; H 6.39.

SUMMARY

1. By preparing β-(selenoyl-2)-propionic acid, the authors have demonstrated the possibility of acylating selenophene with acyloxysilanes from dicarboxylic acids.

2. A method has been worked out for the preparation of keto acids of the selenophene series by acylation of selenophene with acyloxysilanes obtained from the monoethyl esters of dicarboxylic acids, in the presence of anhydrous lead chloride. Using this method, the authors have prepared for the first time the following keto acids: β-(selenoyl-2)-propionic, δ-(selenoyl-2)-valeric, η-(selenoyl-2)-caprylic and ν-(selenoyl-2)-pelargonic acids.

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CATALYTIC TRANSFORMATIONS OF TERPENES

VII. PREPARATION OF OPTICALLY PURE α-PINENE FROM β-PINENE

G. A. Rudakov and M. M. Shestaeva

Investigations which have been carried out to date have not permitted a reliable determination of the optical rotation of optically pure α-pinene. Thurber and Thielke [1] obtained optically active α-pinene ($[\alpha]_D^{20}$ + 51.1° and − 51.3°, n_D^{20} 1.4663, d^{20} 0.8592) from its optically active nitrosochloride, separated from its racemic form by the method of Lynn [2]. This sample of α-pinene had a higher optical rotation than all other samples obtained previously; however, its optical purity was not proved, since it has not been established whether Lynn's method ensures complete separation of the racemic and optically active forms of nitrosochlorides of pinene. In addition, from a comparison of the physical constants of α-pinene obtained by Thurber and Thielke with the physical constants of chemically pure α-pinene (n_D^{20} 1.4653 [3], n_D^{25} 1.4631 [4], d_4^{20} 0.8578 [3], d_4^{25} 0.8539 [4]), it was obvious that the first sample contained small impurities, the presence of which could have an effect on the optical rotation of α-pinene.

It was likewise impossible to reach any conclusions with respect to the magnitude of the optical rotation of optically pure α-pinene by making reference to the optical rotation of samples of α-pinene possessing the highest optical activity (samples prepared from natural sources), because in this case it was impossible to ascertain the absence of the racemic form as impurity. From the magnitude of the optical rotation of α-pinene obtained from natural sources, it is possible only to estimate the purity of the preparations of α-pinene obtained by special methods: the optical rotation of such a "natural" sample should not exceed the rotations of the latter samples if they are optically pure. As a rule, the optical rotation of α-pinene prepared from natural sources satisfies this condition. A higher optical rotation was observed only in one case by Brigs and Taylor [5], but according to the authors, the pinene in this case was not absolutely pure and allegedly contained camphene as impurity.

The object of the present investigation was to obtain a reliable value for the optical rotation of optically pure α-pinene. For this purpose it was decided to prepare optically pure α-pinene by a method different from that used by Thurber and Thielke. The starting material for the preparation of optically pure α-pinene was β-pinene. The reason for this choice was that β-pinene, found in the rosin and essential oils of firs, has a constant optical rotation $[\alpha]_D$ − 22.6°, and is generally regarded as optically pure terpene [6], while its transformation into α-pinene does not affect the asymmetric C-atom. The experimental conditions for this reaction have been described [7]. In the present work, the preparation and separation of the terpenes was carried out on a high-efficiency rectifying apparatus. Also, the amount and nature of some negligible impurities in the starting β-pinene, and in the α-pinene, obtained from the isomerization products, were taken into account in order to introduce corrections in the determination of the optical rotation.

In the case of α-pinene obtained by the method described, the value determined for the optical rotation was $[\alpha]_D^{20}$ − 50.1°. The difference between this value and the optical rotation of α-pinene obtained from optically active nitrosochloride amounts to only 2% and is within the limits of experimental error. The fact that similar, closely corresponding results were obtained in other attempts to prepare optically pure α-pinene by different methods leads us to the conclusion that both Thurber and Thielke and ourselves have succeeded in preparing optically pure α-pinene. Accordingly, the value of $[\alpha]_D^{20} = \pm\ 50.6 \pm 0.5°$ may be taken as the most reliable value for the optical rotation of optically pure α-pinene, being the mean value of our own determinations and of those of Thurber and Thielke.

EXPERIMENTAL

All polarimetric determinations were carried out in the triple-plane polarimeter of Schmidt and Hensch. The accuracy of the readings of the polarimeter and of the monochromator was first checked with quartz discs whose optical rotation was determined in the D. I. Mendeleev All-Union (Metrological Research Institute. The length of the polarimeter tube, 49.8 mm, was checked by means of beam compasses.

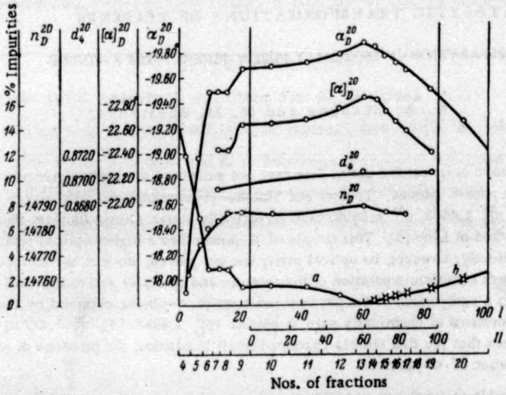

Fig. 1. Isolation and characteristics of β-pinene sample No. 1.
I) Amount distilled (in %); II) amount of β-pinene distilled, used for isomerization (in %).
a) % content of α-pinene, $[\alpha]_D^{20}$ −7.86°; b) % content of Δ^3-carene, $[\alpha]_D^{20}$ +17.5°.

The starting material used for the isolation of α-pinene was turpentine, obtained from rosin of the common fir (Picea excelsa LK) [8,9]. In order to avoid the mutual transformations α-pinene ⇌ β-pinene by the catalytic action of rosin acids [7], the rosin was submitted to treatment with alkali: to 100 g of rosin was added 35 g of 30% of NaOH, the mixture was stirred, and the turpentine was steam distilled. From 4,770 g of rosin was obtained 514 g of turpentine, n_D^{20} 1.4736, $[\alpha]_D$ − 14.06°. The turpentine was submitted to analytical fractionation and was found to contain α-pinene ($[\alpha]_D^{20}$ − 7.86°), β-pinene, Δ^3-carene, limonene, sesquiterpenes, and terpenoid alcohols. In order to isolate the β-pinene, the turpentine was subjected to a number of fractionations on a column backed with nichrome spirals, and equivalent to about 50 theoretical plates. Two samples of β-pinene were thus obtained:

Sample No. 1. (43 g), n_D^{20} 1.4786, d_4^{20} 0.8701, $[\alpha]_C^{20}$ −19.42°, $[\alpha]_D^{20}$ −22.55°, $[\alpha]_J^{20}$ −23.29°, $[\alpha]_V^{20}$ −24.62°, $[\alpha]_F^{20}$ −26.66°, $[\alpha]_i^{20}$ −25.02°.
Sample No. 2. (52 g), n_D^{20} 1.4781, d_4^{20} 0.8697, $[\alpha]_D^{20}$ −20.76°.

The amount and nature of the impurities contained in these two samples of β-pinene are shown on the fractionation curves (Figs. 1 and 2). In the initial fractions having a lowered optical rotation, α-pinene is contained as impurity. The amount of these terpenes in each fraction was calculated, using the equation of Biot, taking the values of $[\alpha]_D^{20}$ −7.86° for α-pinene, and $[\alpha]_D^{20}$ +17.5° for Δ^3-carene [10]. The content of limonene was neglected. The results of determinations of α-pinene were added and the % content of α-pinene with $[\alpha]_D^{20}$ −7.86° in the original β-pinene having been taken into account, corrections were introduced into the optical rotation of α-pinene obtained by the isomerization of β-pinene. Since the presence of Δ^3-carene as impurity could not have affected the final result of the determination, because Δ^3-carene and its isomerization

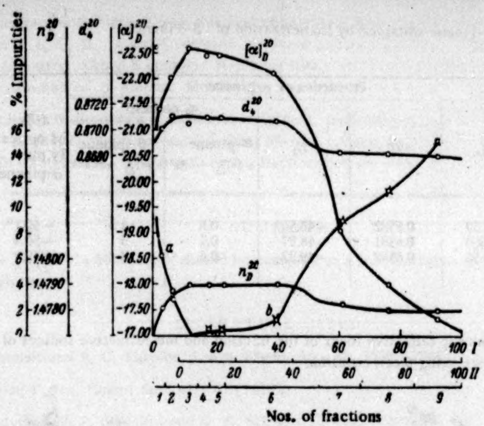

Fig. 2. Isolation and characteristics of β-pinene sample No. 2. I) Amount distilled (in %); II) amount of β-pinene distilled, used for isomerization (in %).
a) % content of α-pinene, $[\alpha]_D^{20}$ −7.86°; b) % content of Δ^3-carene, $[\alpha]_D^{20}$ +17.5°.

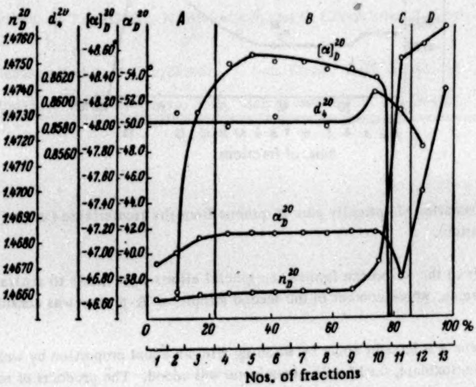

Fig. 3. Isolation of optically pure α-pinene from the products of isomerization.

Properties of α-Pinene Obtained by Isomerization of β-Pinene.

Nos. of samples of β-pinene	Properties of α-pinene					$[\alpha]_D^{20}$ of optically pure α-pinene
	n_D^{20}	d_4^{20}	$[\alpha]_D^{20}$	% content		
				α-pinene c $[\alpha]_D^{20}$ −7.86°	β-pinene c $[\alpha]_D^{20}$ −22.8°*	
1	1.4659	0.8582	−48.56°	0.8	4.5	−50.1°
2	1.4660	0.8581	−48.97	0.1	5	−50.4
1 + 2	1.4656	0.8582	−49.22	0.4	2	−49.9

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* Calculated from the refractive index of the fraction and the refractive indices of pure α- and β-pinenes, using Biot's equation.

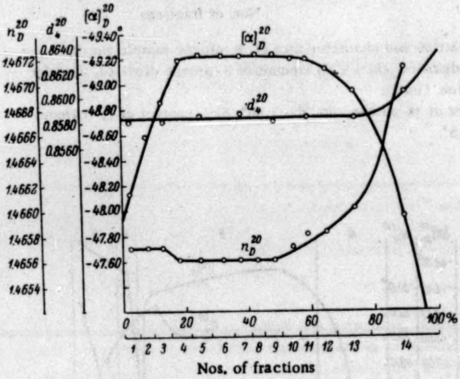

Fig. 4. Isolation of optically pure α-pinene from the isomerizate (second fractionation).

products are easily separated from the α-pinene formed, no special efforts were made to separate completely the β-pinene from the Δ^3-carene, whose content in the second sample of β-pinene was considerable (approximately 6%).

Isomerization of β-pinene was brought about by warming with an equal proportion by weight of benzoic acid at 125° for 20 hours. As antioxidant, 0.01% of hydroquinone was added. The products of reaction were steam distilled. From the first sample of β-pinene was obtained 33 g of distilled isomerization product, hereinafter referred to as product No. 1. From the second sample of β-pinene was obtained 31 g of isomerization product (No. 2). The isomerizates had the following properties:

No. 1: n_D^{20} 1.4687, d_4^{20} 0.8616, $[\alpha]_D^{20}$ −49.27; No. 2: n_D^{20} 1.4697, d_4^{20} 0.8601, $[\alpha]_D^{20}$ −46.76°.

It was established by analysis [11] that the isomerizates did not contain camphene.

Both isomerizates were subjected to fractionation on the column described. As the α-pinene obtained from both isomerizates contained the same impurities, data are given only for the fractionation of isomerizate

No. 1 (Fig. 3). The fractions obtained from this isomerizate have been divided into four groups, denoted in Fig. 3 by the letters A, B, C, D. Group A contains α-pinene and an unidentified hydrocarbon with a lower optical rotation as impurity. Group B contains α-pinene with a small proportion of β-pinene. Group C contains a considerable amount of β-pinene. Monocyclic terpenes mainly are contained in Group D.

The characteristics of the purest fractions of α-pinene, isolated from isomerizates No. 1 and No. 2, are given in the table. As the α-pinene contained about 5% of β-pinene, Fractions 4-10 of both isomerizates were combined and again fractionated. The results of this fractionation are shown graphically in Fig. 4 and in the table.

SUMMARY

The value of $[\alpha]_D^{20} = \pm 50.6° \pm 0.5°$ should be accepted as a reliable value for the optical rotation of optically pure α-pinene.

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* T.p. = C. B. Translation pagination.

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(1) R. H. [illegible], J. Am. Chem. [illegible]

(2) R. V. [illegible], Anal. Chem. [illegible]

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(4) [illegible], J. Am. Chem. Soc. [illegible]

(5) [illegible], J. Phys. Chem. [illegible]

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PHYSICAL PROPERTIES OF CAMPHENE

G. A. Rudakov and M. M. Shestaeva

Physical constants of camphene quoted in the literature vary within very wide limits. For example, the melting points of camphene given vary from 40 to 55° [1]. An analysis of the causes of these divergencies in the physical constants of camphene, as established by various workers, leads us to the conclusion that these differences are due to most of the camphene preparations described having been insufficiently purified. Irrespective of the method used in its preparation, camphene usually contains as impurities other terpenes with boiling points close to its own. Separation of camphene from these impurities may be carried out successfully by distillation, using high efficiency laboratory fractionating columns. However, this method of purification has been used in the laboratory only comparatively recently, and has not been used by most of the workers who have prepared camphene.

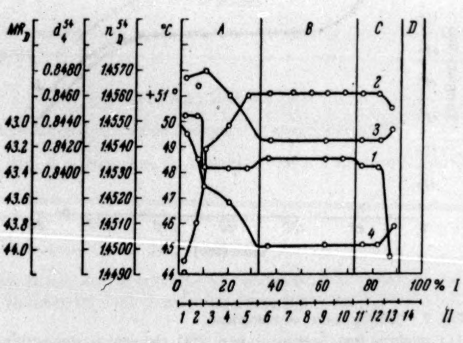

Fig. 1. Fractionation of camphene prepared by dehydration of isoborneol with sulfuric acid. I) Amount distilled (in %); II) Nos. of fractions. 1) Freezing point, 2) n_D^{54}, 3) d_4^{54}, 4) MR_D. A) Camphene and tricyclic terpenes; B) pure camphene; C) camphene containing high-boiling substances as impurities; D) distillation residue.

The present investigation has been undertaken with the object of establishing the most reliable data for the more important physical constants of camphene, which are indispensable in scientific and technical investigations. For this purpose three samples of camphene have been subjected to careful purification: natural camphene separated from the essential oil from the Siberian fir (Abies sibirica) and two synthetic samples, one of which was obtained by dehydration of isoborneol, and the other by catalytic isomerization of pinene.

The physical properties of the samples of camphene mentioned differed considerably before purification, but were found to be identical after purification (see table). Both the fractionation curves (one of which is shown in Fig. 1 as an example), and the cooling curves of the purified camphene samples exhibited regions which are characteristic of products of sufficient purity (Fig. 2). In this respect, the cooling curves of the purified samples differed sharply from the cooling curves of insufficiently purified samples of camphene, although in some cases the latter had higher melting points (camphene obtained from isoborneol).

Origin of camphene	Temperatures			n^{54}_D	d^{54}_4	MR_D	$[\alpha]_D$*
	Freezing point	Melting point	Boiling point (761.2 mm)				
From essential oil of the fir	+48.2°	+49.5°	—	1.4564	0.8412	44.05	−106.21
Dehydration of isoborneol	+48.5	+49.5	158.5°	1.4561	0.8426	43.98	—
Catalytic isomerization of pinene	+48.5	+49.0	158.5	1.4564	0.8425	43.99	+56.21

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* In benzene c ~ 40.

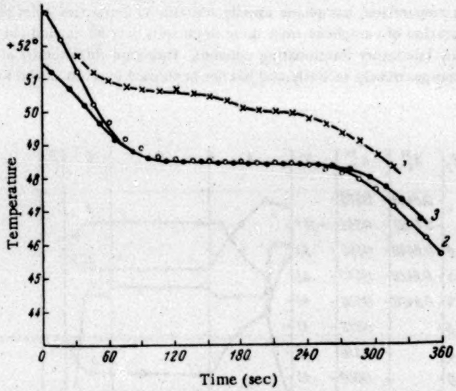

Fig. 2. Cooling curves of camphene.
1) Camphene from isoborneol, m.p. 211° (by dehydration with sulfuric acid), steam distilled; 2) the same camphene redistilled on a fractionating column equivalent to about 50 theoretical plates (Fig. 1, fraction No. 9); 3) camphene prepared by isomerization of α-pinene.

It must be mentioned that the physical data for camphene obtained by us are very close to those obtained by a group of American chemists [2] who have purified camphene, using high-efficiency rectifying columns.

The optical rotation of camphene is usually determined in benzene solutions and less often in alcoholic or toluene solutions. Hückel [3] and co-workers have established the relationship between specific optical rotations of camphene measured in benzene and alcoholic solutions. In the present investigation, we have established the relationship between specific optical rotations of camphene in benzene, toluene and racemic pinene solutions. The values obtained for camphene prepared by catalytic isomerization of α-pinene were: $[\alpha]_D$ + 54.51° (in benzene c = 42), $[\alpha]_D$ + 54.03° (in toluene c = 42), $[\alpha]_D$ + 53.15° (in racemic pinene c = 40).

EXPERIMENTAL

Camphene from essential oil of the Siberian fir (Abies sibirica). 3.5 kg of the essential oil was fractionated on a column equivalent to about 30 theoretical plates. The crude camphene obtained was again fractionated, once on a column equivalent to about 30, and a second time on a column equivalent to about 50 theoretical plates.

Camphene from isoborneol. Isoborneol (m.p. 211°) obtained from technical isoborneol by repeated recrystallization from alcohol, was dehydrated with sulfuric acid [4]. The camphene obtained had m.p. 52°, f. p. 50.7°, n_D^{54} 1.4559, d_4^{54} 0.8526, and was distilled on a column equivalent to about 50 theoretical plates. 60 g of camphene was taken for distillation. The course of the runs is shown by means of curves in Fig. 1.

Camphene prepared by catalytic isomerization of α-pinene. Catalytic isomerization of pinene was carried out in the presence of titanic acid at 100°. The reaction products were fractionated on a column equivalent to about 30 theoretical plates, yielding among others, tricyclic terpenes and unreacted pinene, in addition to camphene. Pinene was then removed by selective oxidation with $KMnO_4$ in alkaline solution. The crude camphene obtained, m.p. 32°, n_D^{54} 1.4546, $[\alpha]_D$ +51.5° (in benzene), was fractionated on a column equivalent to about 50 theoretical plates.

Determination of the physical constants of camphene. Freezing points were determined from cooling curves in a thick-walled test tube, diameter 20 mm, using a sample of about 3 g. The temperatures were measured with a short thermometer having divisions of 0.5°. Melting points were determined in the Thiele apparatus, and boiling points in the ebullioscope of Swientoslawski [5], using a normal thermometer with a scale of 150-200°, having divisions of 0.1°. Refractive indices were determined in the Abbe (Zeiss) refractometer, optical rotations in the triple-plane polarimeter (Schmidt and Hensch). In temperature determinations, corrections were introduced to account for variations in the height of the mercury column.

SUMMARY

The following physical constants may be taken as the most reliable data for camphene: f.p. 48.5°, b.p. 158.5°, n_D^{54} 1.4564, d_4^{54} 0.8421.

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EXPERIMENTAL

Camphene from essential oil of the Siberian fir (Abies sibirica). 3.5 kg of the essential oil was fractionated on a column equivalent to about 35 theoretical plates. The crude camphene obtained was again fractionated, first on a column equivalent to about 25, and a second time on a column equivalent to about 60 theoretical plates.

Camphene from isoborneol. Isoborneol (m.p. 212°) obtained from technical isoborneol by repeated recrystallization from alcohol, was dehydrated with sulfuric acid [5]. The camphene obtained had m.p. 50°, [illegible] $n_D^{[illegible]}$ 1.4555, $d_4^{[illegible]}$ 0.8456, and was distilled on a column equivalent to about 60 theoretical plates. 30 g of camphene was taken for distillation. The course of the test is shown by means of curves in Fig. 1.

Camphene prepared by catalytic isomerization of α-pinene. Catalytic isomerization of pinene was carried out for the purpose of [illegible]. The reaction products were fractionated on a column equivalent to about 30 theoretical plates, yielding, among others, tricyclene, terpenes and unsaturated products, in addition to camphene. Pinene was then removed by selective oxidation with $KMnO_4$ in alkaline solution. The crude camphene obtained, m.p. 33°, $n_D^{[illegible]}$ 1.45[illegible], $[\alpha]_D$ +51.5° (in benzene), was fractionated on a column equivalent to about 60 theoretical plates.

Determination of the physical constants of camphene. Freezing points were determined from cooling curves in a thick-walled test tube, diameter 25 mm, using a sample of about 5 g. The temperatures were measured with a short thermometer having divisions of 0.2°. Melting points were determined in the Thiele apparatus, and boiling points in the ebulliometer of Swietoslawski [5], using a normal thermometer with a scale of 150-200°, having divisions of 0.1°. Refractive indices were determined in the Abbe (Zeiss) refractometer, optical rotations in the circle-plane polarimeter (Schmidt and Haensch). In temperature determinations, corrections were introduced to account for variations in the height of the mercury column.

SUMMARY

The following physical constants may be taken as the most reliable data for camphene: f.p. 46.5°, b.p. [illegible], $n_D^{[illegible]}$ 1.4555, $d_4^{[illegible]}$ 0.8422.

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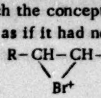
DISCUSSION

CONCERNING PAPERS BY A. I. TITOV AND F. L. MAKLYAEV

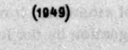
E. A. Shilov

A. I. Titov and F. L. Maklyaev have recently published four papers under the general title: "Conjugated addition reactions of halogens to olefins" [1,2]. These papers contain certain statements concerning the theory of ionic addition reactions, which call for the following comments.

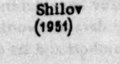
1. In their introductory paper, Titov and Maklyaev outline their views on the mechanism of mixed addition reactions, presenting them as a new and original theory. In fact, however, the ideas expressed by them have already been put forward earlier by others and may be regarded as well-known, at least among organic chemists interested in the theory of ionic reactions. This applies in particular to the hypothesis of the π-complex which Titov and Maklyaev now postulate anew, although it has already been formulated by Dewar [3] in 1946 and was also suggested by Price [4] and by myself [5] at that time. In fact, the concept of a complex of this nature was put forward earlier still [6], but it was at first applied (in the form of a resonance theory) to complexes between olefins and salts of heavy metals. In the course of the last ten years, the concept of the π-complex has been expanded or mentioned in a number of papers [7,8], and it continues to be a subject for discussion.

Titov and Maklyaev make no mention of papers in which the concept of the π-complex has been dealt with. They merely touch on Dewar's hypothesis, and they present it as if it had no connection with their own concepts. In fact, they quote the cation formula of Roberts and Kimbal:  $\mathrm{R{-}CH{-}CH{-}R}$ (bridged by $\mathrm{Br^{+}}$), and add the remark: "Dewar's views are in agreement with this hypothesis" [1a]. This is as far as Titov and Maklyaev go in their review of the literature on the π-complex.

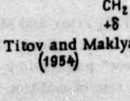
There is, however, a fundamental difference between the π-complex and the cation of Roberts and Kimbal: in the case of the π-complex the theory postulates the existence of coordinate, and not covalent, linkage, the π-electrons having the same function as the electron doublet of amines entering into coordination complexes. When applied to the interpretation of mechanisms of chemical reactions, the hypothesis of Roberts and Kimbal leads to difficulties which are not encountered with the concept of the π-complex [5]. Besides, the π-complex postulated by Titov and Maklyaev does not essentially differ from the π-complex as it is generally understood. The difference merely lies in the typographic signs used to represent the π-complex. For example:



Dewar
(1949)

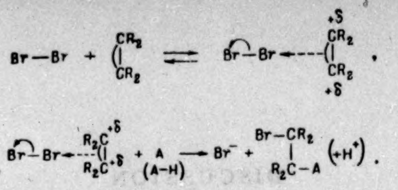


Shilov
(1951)

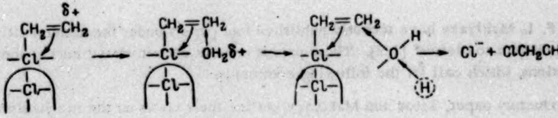


Titov and Maklyaev
(1954)

2. Having thus ascribed to themselves the origination of the concept of the π-complex, Titov and Maklyaev attempt to show that they have produced, as it were, a new theory of the formation of mixed compounds during the halogenation of olefins (or, to use their term, a theory of "conjugated addition reactions of halogens"). This theory is expressed in two equations:



It will be seen that this is no new theory, but the long-known trimolecular donor-acceptor mechanism of mixed addition reactions. The original concept of this theory is obviously due to Robinson [10], who as far back as 1932 formulated the following mechanism of the formation of 2-chloroethanol from chlorine, water and ethylene:



The mechanism which I put forward in my paper in 1936 [11] contains the essential elements of the contemporary theory of electrophilic addition reactions, including inexplicitly also the π-complex. Subsequently, the trimolecular addition mechanism has appeared many times in Soviet and foreign journals [12,7,8] with certain improvements and variations in its presentation. Titov and Maklyaev, however, present this mechanism as if it were a product of their own ideas, for which other authors have merely provided odd experimental data.

3. When they discuss mixed addition reactions in general, Titov and Maklyaev connect these reactions with the theory of N. A. Shilov and call them "conjugated addition reactions of halogens to olefins." As is well known, N. A. Shilov introduced the term "concurrent reactions" for two parallel reactions, one of which excites the other. The mixed addition reaction, according to the donor-acceptor mechanism, does in fact consist of two stages of one reaction.

It is therefore inexpedient to extend the term "conjugated reactions" to heterolytic addition reactions. If it is necessary to use some special term for such reactions, one might follow Swain [13] and call them "concerted" reactions. Personally, however, I prefer the more concrete term – acceptor-donor reactions.

4. When Titov and Maklyaev attempt to apply the "theory of conjugated reactions" to the interpretation of chemical facts, they meet with failure. Thus, the formation of trans-chlorovinyl-mercurichloride from corrosive sublimate and acetylene is not the result of the addition of $HgCl^+$ and Cl^-, as interpreted by the authors [1b], but is due to the action of $HgCl_2$ and Cl^- on $HC\equiv CH$, in accordance with the general acceptor-donor mechanism [14]. Cis-chlorovinylmercurichloride is not formed in the gaseous phase, but on the solid surface of Cis-chlorovinylmercurichloride [15]. The acceleration of the bromination of benzene as a result of the addition of sulfuric acid to bromine water is to be explained as being due not to the addition of a molecule of sulfuric acid to bromine [1c], but rather to the formation of the bromine cation from HOBr and the hydrogen ion [16]. Substitution of hydrogen at the double bond in olefins by chlorine proceeds mostly by the radical mechanism, rather than by the heterolytic mechanism. It is obvious that Titov and Maklyaev have not acquainted themselves with the literature discussing the reactions with which they deal.

5. In one of their papers [1d] Titov and Maklyaev have determined the relative activity of third components in certain trimolecular addition reactions. These data are worthy of attention. It must, however, be admitted that the term "activity coefficient" proposed by the authors and its designation by the letter f (e.g. f_{H_2O}) are not successful choices. The relative rate of addition of anions is not some natural constant, but varies from one reaction to another. Besides, this term and symbol are used, as is well known, in chemical thermodynamics in a totally different sense. All that is necessary in this case is to simply state the relative activity of the third components in different reactions without having to use any special symbol (cf. [17]), as is the practice in considerations of other kinetic series or in the case of compounds forming a series from energy considerations.

Other experimental results described in the papers of Titov and Maklyaev are of interest from the point of view of preparative chemistry. The authors have prepared several complex esters of 2-chloroethanol by the simultaneous action of ethylene and chlorine on concentrated acids. By a similar method they have prepared chloroethyl substitution products of benzosulfonamide. From the point of view of theory these reactions may serve as good examples of donor-acceptor reactions.

The works of Titov and Maklyaev here discussed do not introduce any new general ideas into science.

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LETTERS TO THE EDITOR

I.

Remarks concerning the paper by A. K. Plisov and N. S. Skornyakov, "Configuration and properties of unsaturated acids and their derivatives. IV. Oxidation of octadecenoic acids and their esters."

The paper by A. K. Plisov and N. S. Skornyakov which has just appeared [J. Gen. Chem. 26, 59 (1956) (T.p. 57)*] compels me to make the following comments.

The authors of this paper produce data on the relative oxidation of oleic, elaidic, petroselinic and petroselaidic acids with benzoyl hydroperoxide. They draw the conclusion that there is a difference in the reactivity of geometrically isomeric acids and of their esters. Unfortunately, the authors have not noticed our communication [J. Gen. Chem. 22, 1140 (1952)] (T.p. 1187)*, dealing with the same problem. In that paper we have provided data relating to the relative oxidation of petroselinic and petroselaidic acids with benzoyl hydroperoxide, as well as data on their hydrogenation, and we have made certain relevant conclusions with regard to the behavior of cis- and trans-isomerides.

G. V. Pigulevsky

II.

In 1948 my paper, "8-Substituted derivatives of methyl-xanthines", was published in J. Gen. Chem. 18, No. 12, 2129. It is only now that a very important numerical mistake in the experimental part has come to my notice. This mistake concerns the method of preparation of the basic starting material for a whole series of preparations. The mistake makes the paper useless and throws doubts as to the reliability of the experimental data. It is essential that the mistake be corrected, because the paper in question is the first of a series of communications (eight in all) which have been published in subsequent years. I would be very much obliged to have the following correction published:

Page	Line	Printed	Should read
2129	21 from top	26 g $KMnO_4$	16 g $KMnO_4$

E. S. Golovchinskaya

III.

Through an error on the part of the authors, a mistake has crept into the paper by A. V. Lapitsky, L. N. Shishkina, M. A. Pchelkina and B. A. Stepanov, "Investigation of the solubility of anhydrous meta-niobates of alkali metals" [J. Gen. Chem. 25, 1865 (1955)], which we would ask to have corrected.

Original page	Line	C.B. Translation page	Line	Printed	Should read
1865	5 from top	1807	4 from bottom	$SP = 5.06 \cdot 10^{-8}$	$SP = 1.21 \cdot 10^{-8}$

A. V. Lapitsky

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* T.p. = C. B. Translation pagination.

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